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PART I: INVESTIGATION OF ENDOCYCLIC NUCLEOPHILIC SUBSTITUTION AT DI- AND TETRA-COORDINATE SULFUR PART II: SYNTHESIS OF 3-TOSYL-1,2,3-BENZOXATHIAZOLE-2,2-DIOXIDE AND ITS REACTIONS WITH NUCLEOPHILES

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A DISSERTATION

Submitted to the University of New Hampshire
in Partial Fulfillment of
the Requirements for the Degree of

Doctor of Philosophy
in
Chemistry

December, 1985

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PART II: SYNTHESIS OF 3-TOSYL-1,2,3-BENZOXATHIAZOLE-2,2-DIOXIDE AND ITS REACTIONS WITH NUCLEOPHILES.

by

Sumalee Chumpradit
University of New Hampshire, December, 1985

Part I: Bis-2-(4'-toluenesulfonyl)methylphenyl disulfide, bis-2-aminophenyl disulfide, 2'-methylsulfonylphenyl 4-toluenesulfonate and N-methyl-N-(2'-aminobenzyl)-4-toluenesulfonamide, all of which appeared capable of undergoing endocyclic nucleophilic substitution at sulfur, were synthesized. Each compound was treated with the strong base (sodium hydride or n-butyllithium) in THF. No trace of the hoped-for base-induced rearrangement products were found. N-methyl-N-(2'-aminophenyl)-4-toluenesulfonamide and some of its derivatives reacted in part with n-butyllithium via an elimination-addition pathway.

Part II: 3-Tosyl-1,2,3-benzoxathiazole-2,2-dioxide and

its 5-nitro derivative were synthesized. Their rates of base hydrolysis in aqueous acetonitrile were determined. The reaction of the cyclic sulfamate, 3-tosyl-1,2,3-benzoxathiazole -2,2-dioxide with methylamine and tert-butylamine yielded products arising from ring S-N bond cleavage. Phenyllithium, methyllithium and potassium fluoride gave products from exo S-N bond cleavage. Sodium methoxide yielded products from both exo and endo S-N bond cleavage. An amide synthesis utilizing the cyclic sulfamate as a coupling reagent was also demonstrated.

HISTORICAL

PART I

Nucleophilic Substitution at Sulfur

Previous work on nucleophilic substitution at dicoordinate, tricoordinate and tetracoordinate sulfur up to 1978 has been reviewed in Yildiz's dissertation.[1]

Little is known about the nature of intermediates in substitution reactions at dicoordinate sulfur(II). Large steric effects and small substituent effects which have been measured for a variety of reactions have been interpreted as evidence for a direct S_N2 type of displacement with no intermediate. However, the reaction of sulfenyl derivatives with amines in benzene, which is catalyzed by added bases or the nucleophile itself, appears to proceed via an intermediate complex.[2] Since the sulfenyl sulfur cannot be chiral, stereochemical studies involving optically active compounds are not possible.

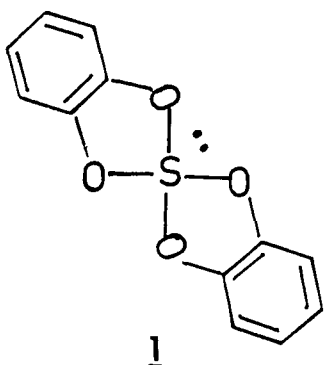
The stereochemistry of nucleophilic substitution at tricoordinate sulfur(IV) has been studied extensively. Inversion is usually observed, but several cases of retention are known.[3]

For tetracoordinate sulfur(VI), only inversion at sulfur has been observed.[3]

At least two mechanisms for nucleophilic substitution

at sulfur have been considered:[4-10] a two-step process via trigonal bipyramidal sulfurane intermediates and a one-step concerted process.

Pentacoordinate intermediates of the two-step process have their counterparts in phosphorus chemistry. Geometries of phosphoranes range from ideal trigonal bipyramids to rectangular pyramids.[11] Pseudopentacoordinated sulfur(IV) compounds such as sulfur tetrafluoride in which one of the coordination sites is occupied by a lone electron pair are common.[12] Several stable sulfuranes, such as 1 ,[13] 2 ,[14] 3 ,[15] 4 , 5 and 6 ,[16,17] (fig 1) have been synthesized and the latter three proposed as intermediates in nucleophilic substitution at sulfur.



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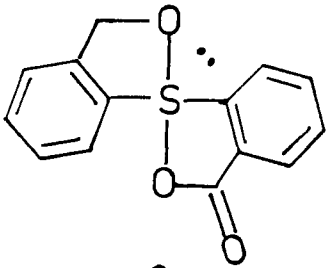

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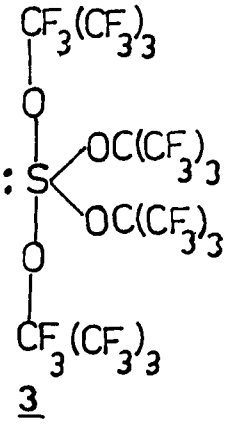

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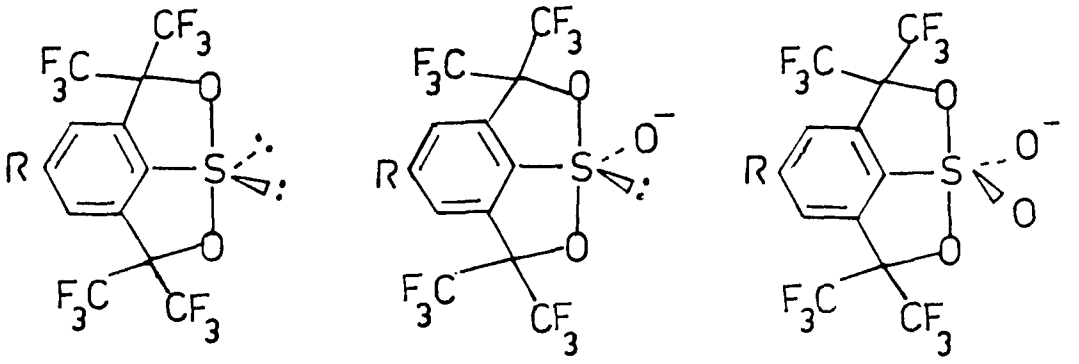
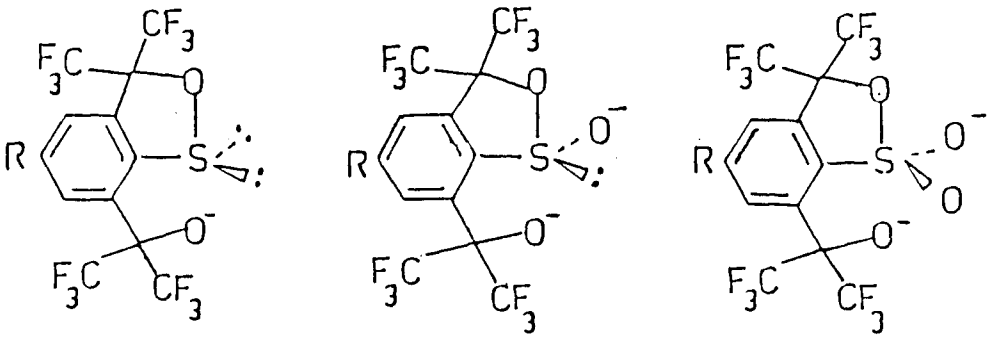


4 5 6

Figure 1.
Structures of stable sulfuranes.

X-ray crystallographic structures of sulfuranes 4 , 5 , and 6 show these species to be trigonal bipyramidal in geometry in the solid state, assuming the sulfur atom electron pairs on 4 and 5 to be ligands.[18] Low temperature NMR spectra and pKa measurements show the importance of hypervalent bonding in the ground state structures of 4 and 5 in solution. By measurement of the pKa value of their open chain conjugated acids, sulfuranes 4 , 5 and 6 were calculated to be at least 31.4, 24.7 and 10.9 kJ/mol more stable than their open chain isomers 7 , 8 and 9 , respectively. Martin and coworkers[18] suggested that the energy differences are due to intramolecular through-space stabilizing interactions which are greater for the hypervalent anions 4 , 5 and 6 than for the open chain analogue 7 , 8 and 9 .[18]



7 8 9

In the cases of 4 , 5 and 6 (fig 1), the preferred configuration would have the nucleophiles and leaving groups in apical positions which would lead to inversion of configuration at sulfur. For example, sulfurane 4 is a model of an intermediate for nucleoplilic substition at dicoordinate sulfur(II), 5 for substitution at tricoordinate sulfur(IV), and 6 for substitution at tetracoordinate sulfur(VI).

Discussions of the sulfurane intermediate pathway have appeared in the literature.[10,19] Mikolajczyk and Drabowicz[3] argued that the two-step mechanism provides a reasonable explanation for both inversion and retention reactions. Their analysis of the various possibilities is as follows: (a) The addition of the nucleophile, Nu, to face abc opposite to the leaving group, L, of tetrahedral sulfur leads to a trigonal bipyramidal sulfurane which has Nu and L in apical positions. Departure of L gives the product with

inversion. (b) Attack at edges ab, ac or bc places Nu and L in equatorial position. Departure of L before any ligand reorganization (pseudorotation) has taken place results in inversion of configuration (fig 2).

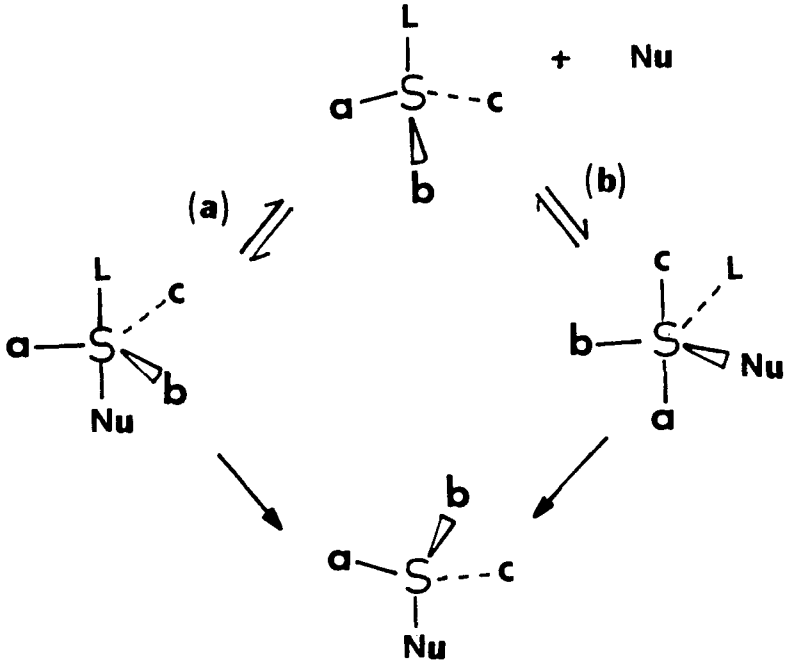


Figure 2.
Substitution at sulfur resulting in inversion of configuration.

Nucleophilic attack at faces abL, acL or bcL, opposite to a substitutuent that is not the leaving group, results in the formation of a sulfurane intermediate having an axial-equatorial arrangement of the nucleophile and the leaving group, respectively. After ligand reorganization, a new sulfurane intermediate is formed in which the leaving

group occupies the apical position from which it departs with retention of configuration (microscopic reversibility)[3] (fig 3).

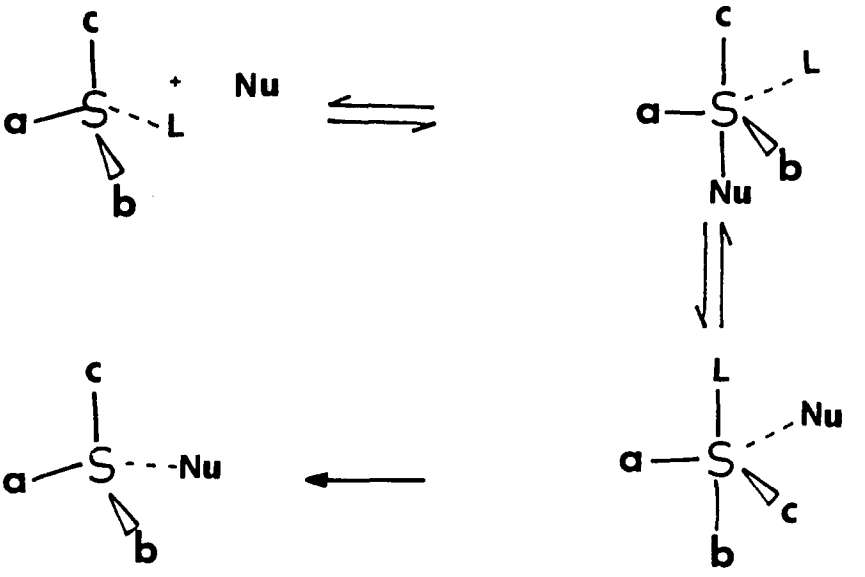
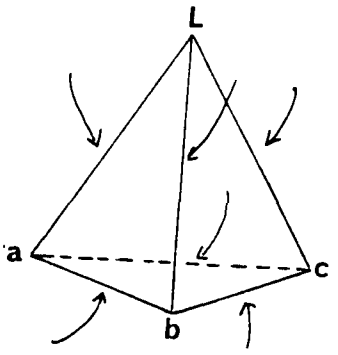


Figure 3.
Nucleophilic substitution at sulfur resulting in retention of configuration.

Another possibility is attack at edges aL, bL or cL to give a sulfurane with L apical and Nu equatorial. Pseudorotation to place L in an equatorial position followed by departure of L leads to a product with retention of configuration (10).



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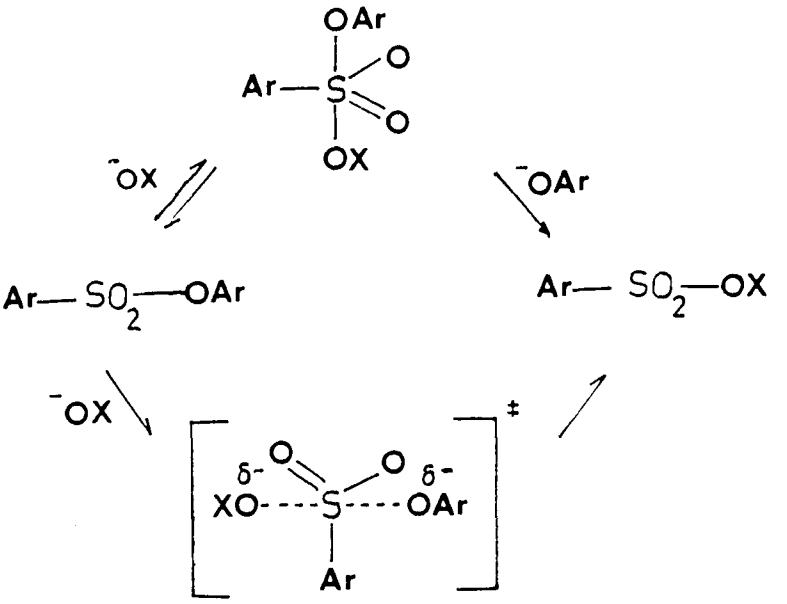
Although sulfurane intermediates have been proposed in many cases, they have not been isolated or directly observed in any nucleophilic substitution reactions, so the question still remains open whether or not they are always, if ever, involved in the process.

Some evidence for the concerted mechanism was reported by Williams and coworkers[20] who found that the reaction of phenolate ion with a series of aryl esters of 4-nitrobenzenesulfonic acid obeyed a linear Bronsted-type relationship (scheme 1).

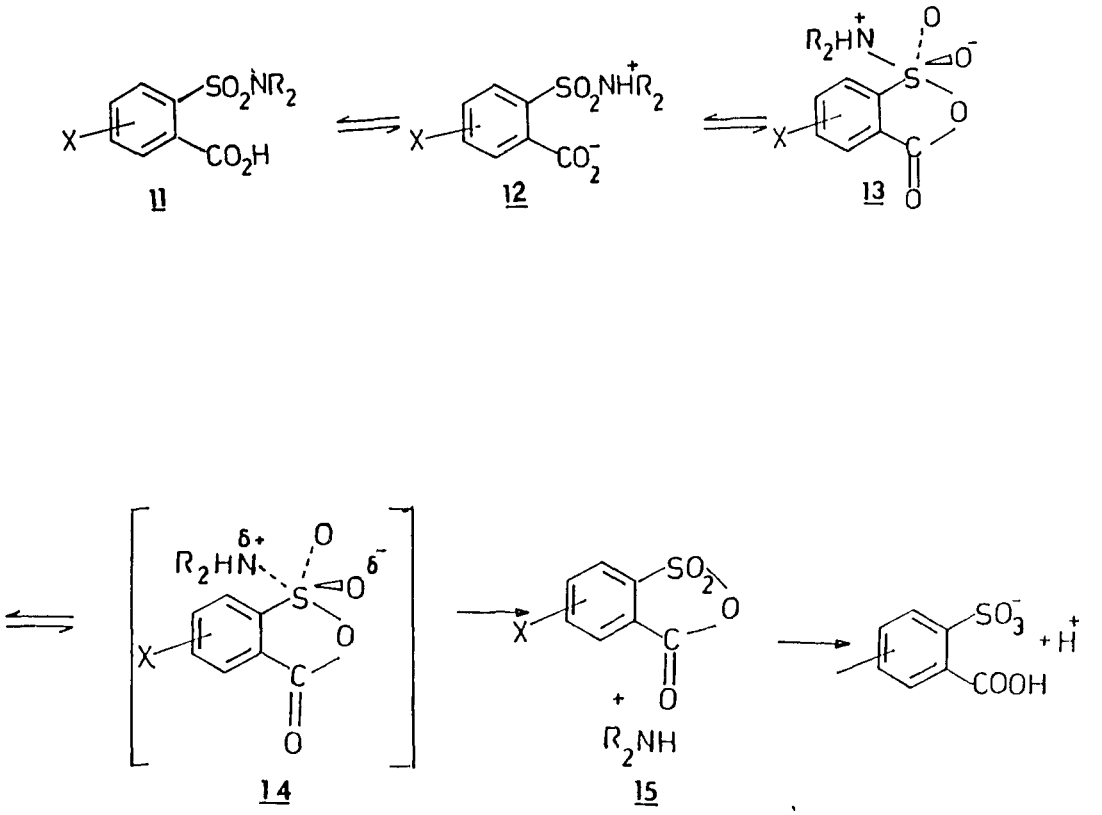


Scheme 1.
Pathways for a sulfonyl transfer reaction.

In this reaction a series of oxyanions with basicities both smaller and larger than the leaving 4-nitrophenolate group were used as nucleophiles. If a stepwise mechanism were followed, a change in the rate-limiting step should occur as the incoming group becomes more or less basic than the leaving 4-nitrophenolate ion. Thus, a nonlinear Brønsted relationship with a break at Δ pK = 0 is expected for the stepwise mechanism which has two electronically distinct transition states. A concerted process with a single transition state should give a linear or gently curving Brønsted correlation. Since it has not yet been possible to confirm the concerted mechanism by other experiments, the possibility can not be excluded that a

very reactive pentacoordinate intermediate is formed in a very shallow well at the apex of the potential energy maximum so that the two transition states have similar electronic structures.

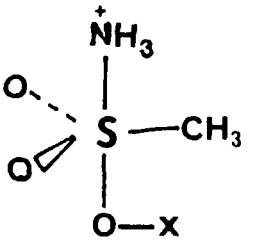
Recently Engberts and coworkers[21-23] proposed a stepwise mechanism for the intramolecular carboxyl-catalyzed hydrolysis of sulfonamides (scheme 2).



Scheme 2.
The stepwise mechanism of intramolecular carboxyl-catalyzed hydrolysis of sulfonamides.

Engberts' main argument for the stepwise mechanism is based on the negative ρ COOH value (-0.54±0.02) for the acid catalyzed hydrolysis of aromatic sulfonamides with substitutuents meta and para to the carboxyl function.[21] This negative value is consistent with a reduction in electron density on the carboxyl group in the transition state compared with the initial state and implies that the new sulfur-oxygen bond is already fully formed in the transition state 14 of the slow step. The sulfur-nitrogen bond, on the other hand, is partially broken. Because the negative value of the leaving group is only a fraction of that for protonation of anilines (ρ = -2.89),[24] the leaving nitrogen must carry only a small partial positive charge in the transition state. The same conclusion applies to the sulfonyl center ($\rho\ SO_2N$ = - - 0.58 + 0.01). The effects of substituents are consistent with a transition state in which all three centers -carboxyl, sulfonamide sulfur and the leaving nitrogen atom- are more electron deficient than in the initial state. The transition state which fits these requirements is that for the breakdown of pentacoordinate intermediate 14 . If S-O bond formation is complete, and S-N cleavage is not, the transition state for a concerted process would be so unsymmetrical[9] as to be scarely distinguishable from 14 . Therefore, the mechanism involves a pentacovalent sulfurane 13 .

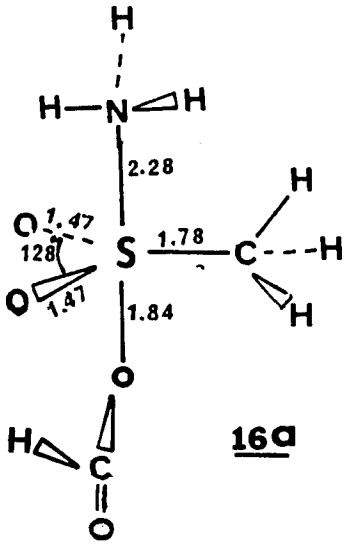
Engberts and coworkers[22] provided further support for this stepwise mechanism by ab initio molecular orbital calculations. By application of the same preference rules to pentacoordinated sulfur compound as those used for comparable phosphorus compounds, the structures 16a and 16b were calculated to be the most favorable ones of the possible structural alternatives. In these structures the rings are attached via apical-equatorial positions and the CSO_{ax} angle is about 90°.



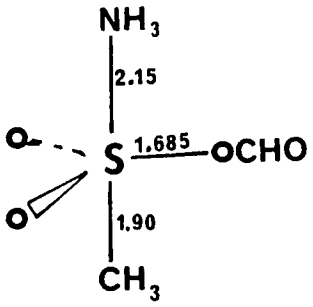
16a, x = CHO

16b, x = H

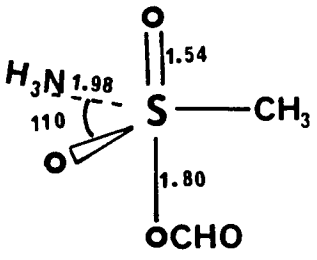
Calculations on the different conformations of this intermediate showed a clear preference for the trigonal bipyramidal structure 16a with apical bonds to the incoming nucleophile and the amine leaving group compared to 17a - c.[22]



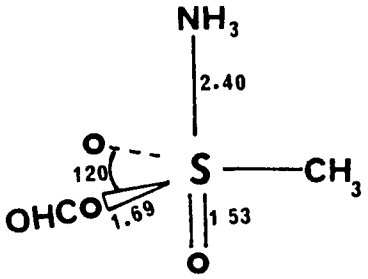
16a



17a



17b

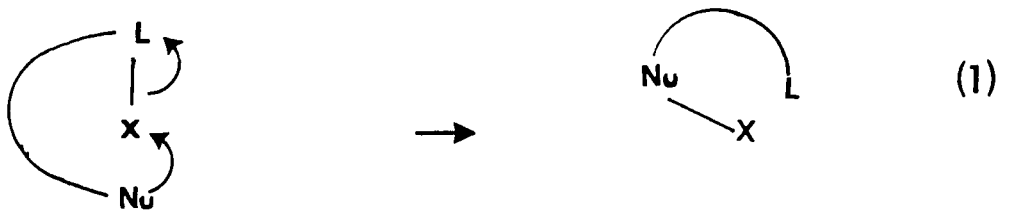


17c

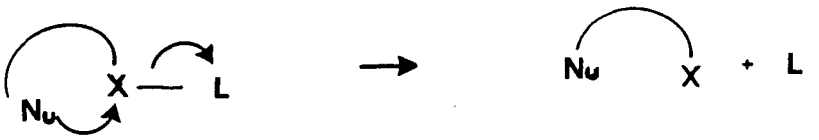
Williams' evidence for a concerted and Engberts' for a stepwise mechanism suggest that sulfonyl transfer reactions may go by either mechanism. It has been established that the analogous phosphoryl transfer reaction can be either concerted or stepwise.[25,26]

Endocyclic Nucleophilic Substitution

Endocyclic nucleophilic substitution is defined as a process in which the leaving group, L, is bonded to the nucleophile, Nu, so that the atom undergoing attack, X, is transfered intramolecularly from L to Nu (eq 1). In contrast, the leaving group is displaced from the parent molecule in an exocyclic substitution process (eq 2).



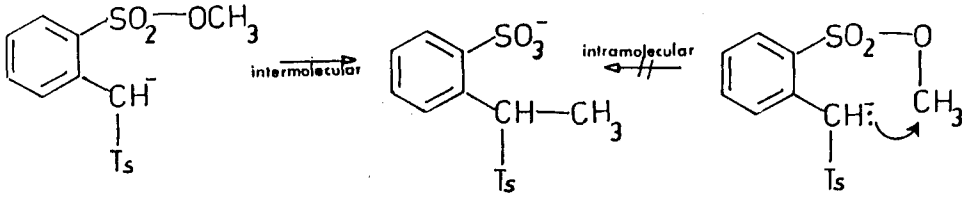
(1)



(2)

Eschenmoser and coworkers[27] investigated endocyclic nucleophilic substitution at a methyl carbon. Their work provided strong evidence that S_N2 reactions at sp^3 carbon take place with stereoelectronic control[28]. The nucleophile must approach the substrate

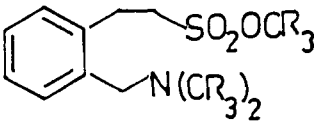
carbon from a 180° angle opposite to the leaving group (scheme 3).



Scheme 3.
Eschenmoser's intramolecular reaction.

Intramolecular endocyclic attack did not occur because a transition state with the proper alignment of the nucleophile and substrate could not be attained.[28] This result also agrees with Baldwin's rule:[29] a six-membered endocyclic process is disfavored.

An example of methyl transfer by endocyclic nucleophilic substitution was reported by King and coworkers.[30] Aminoester 18 at low concentration was converted into betaine 19 partly by way of an intramolecular mechanism, whereas the corresponding reactions of 20 and 21 were entirely intermolecular. The intramolecular reaction pathway observed with 18 decreased with increasing concentration of the starting material.



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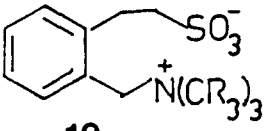

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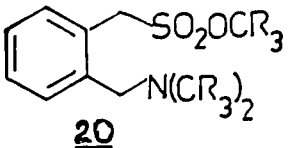

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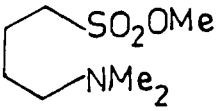
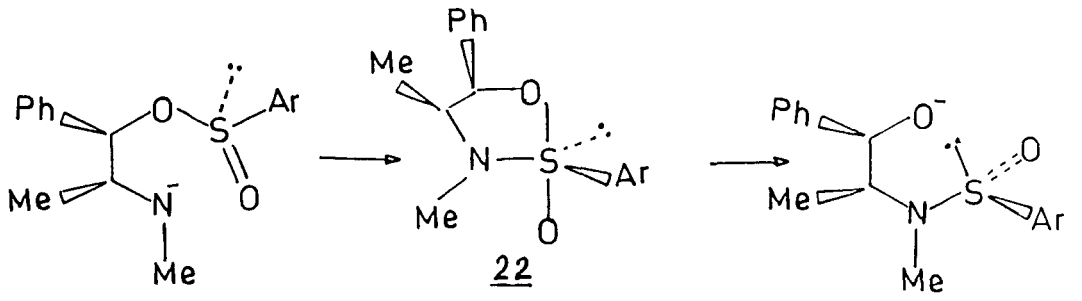


21

Absence of the intramolecular pathway for the reactions of 20 and 21, and the low intramolecular yield for the reaction of 18, are due to the steric strain of an endocyclic reaction proceeding by 8- and 9-membered cyclic intermediates or transition states.[31] This strain is caused by deviation from the ideal 180° orientation of nucleophile, carbon, and leaving group in the eight- and nine-membered cyclic transition states.[30]

Endocyclic nucleophilic substitution at sulfinyl sulfur nas been reported by Wudl.[32] He also demonstrated that intramolecular substitution took place with retention of configuration at low concentrations of the substrate, whereas intermolecular substitution with inversion became evident as starting material concentration was increased (eq 3). The five-membered tetracoordinate sulfurane 22 was proposed as an intermediate.



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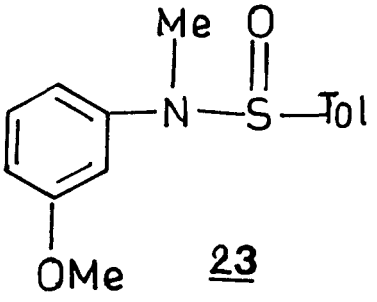
(3)

In a study designed to detect endocyclic substitution sulfinamides 23 were found not to rearrange upon treatment with base, but instead rearranged with acid-catalysis to give anilinosulfoxides 24 .[33] A cross-over experiment showed that the reaction followed an intermolecular mechanism.



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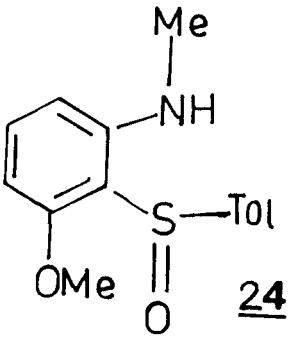
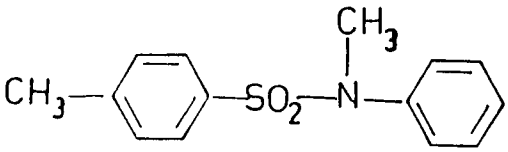


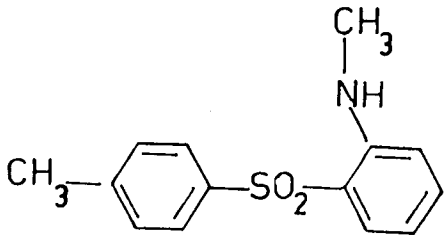
24

Closson,[34] Hellwinkel[35,36] and their coworkers treated arenesulfonamides such as 25a with strong bases

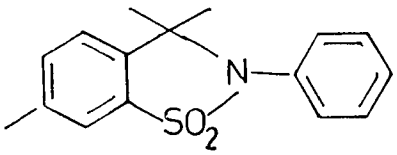
(phenyllithium, n-butyllithium, methyllithium) to obtain sulfones, 25b . An intramolecular mechanism was demonstrated by a cross-over experiment. Hellwinkel obtained 26b by treatment of cyclic sulfonamide 26a with base. This rearrangement must follow an intramolecular endocyclic pathway.



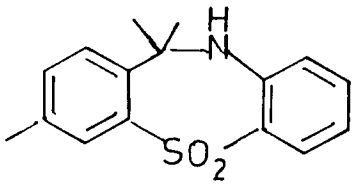
25a



25b



26a



26b

As mentioned earlier, only inversion of configuration has been observed in nucleophilic substitution at tetracoordinate sulfur(VI).[3] Inversion reactions may follow an S_N2 like pathway via a trigonally bipyramidal transition state or intermediate with the nucleophile, sulfur atom and leaving group approximately colinear,[3-5] or they could proceed via a transition

state or intermediate in which nucleophile and leaving group are both equatorial. To see if approximate colinearity of nucleophile, sulfur atom and leaving group is actually necessary for endocyclic nucleophilic substitution at sulfur to occur, Andersen and coworkers[37] synthesized molecules such as 27 - 30 . These molecules appear capable of undergoing endocyclic nucleophilic substitution at sulfur(fig 4).

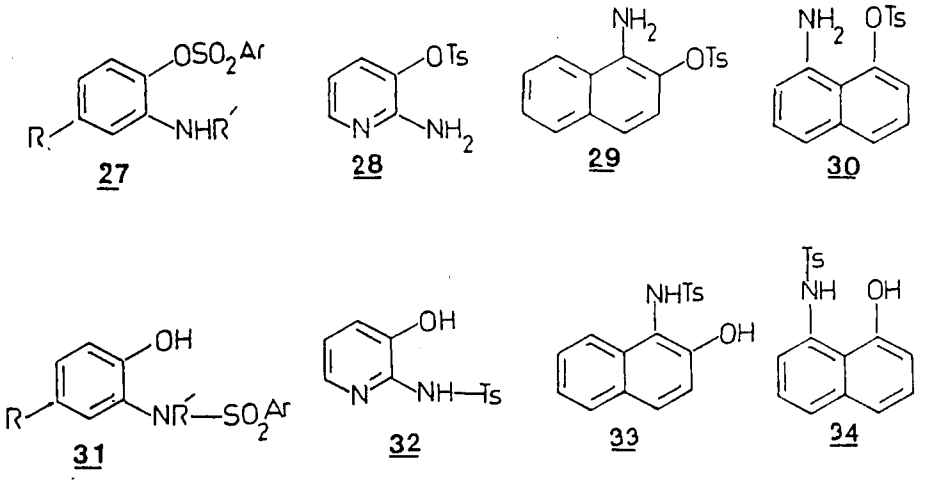
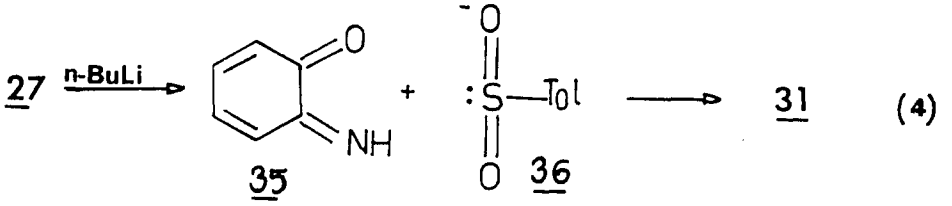
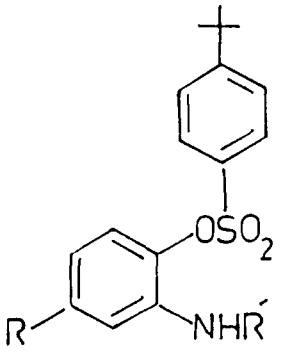


Figure 4.
The structure of aminoaryl arenesulfonates and their rearrangement products.

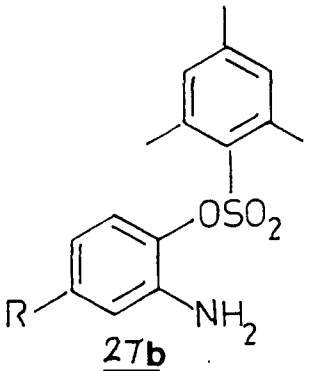
Aminoaryl arenesulfonates 27 - 30 were rearranged intramolecularly upon treatment with strong bases to form hydroxyarylarenesulfonamides 31 - 34 ,respectively (figure 4). Two mechanisms for these rearrangements were considered likely. The first involves endocyclic nucleophilic attack by nitrogen on sulfonyl sulfur with consequent S-O bond cleavage. This rearrangement may proceed through a five- or six-membered transition state or intermediate depending on the structure of the starting material. This mechanism was supported by a cross-over experiment. Another mechanism involves formation of an o-quinonimine(35)- sulfinate(36) pair which collapses to product (eq 4).



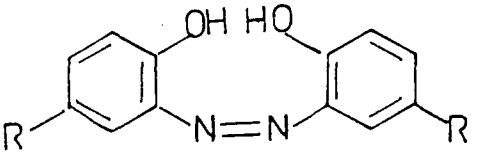
Evidence for this latter mechanism is based on the isolation of azobenzene 37 from the reactions of 27a and 27b with n-BuLi. o-Quinonimine (35) has never been isolated or trapped. This investigation is not yet complete.



27a



27b



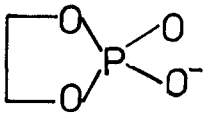
37

In order to provide information about endocyclic nucleophilic substitution at di- and tetra-coordinate sulfur, molecules which appeared capable of undergoing this process were synthesized. Each was then treated with a strong base to create, by deprotonation, an anionic nucleophile seemed capable of attacking the sulfur atom intramolecularly. The resultant reaction products were isolated and identified, and mechanisms for their formation were postulated.

PART II

Kinetic Studies of Alkaline Hydrolysis of Heterocyclic Sulfates

Because of their similarity to molecules of biological interest, the reactivity and stereochemistry of cyclic phosphorus compounds have been extensively studied.[38-40] The five-membered cyclic phosphates 38 - 40 ,[41-44] and phosphonate 42 ,[45] hydrolyze 10^5-10^8 times faster than their open-chain analogues (in acid or base).



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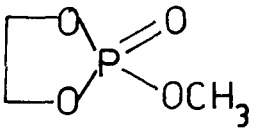

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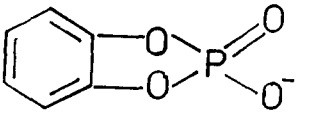

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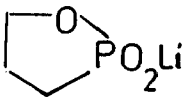

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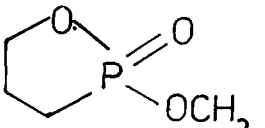
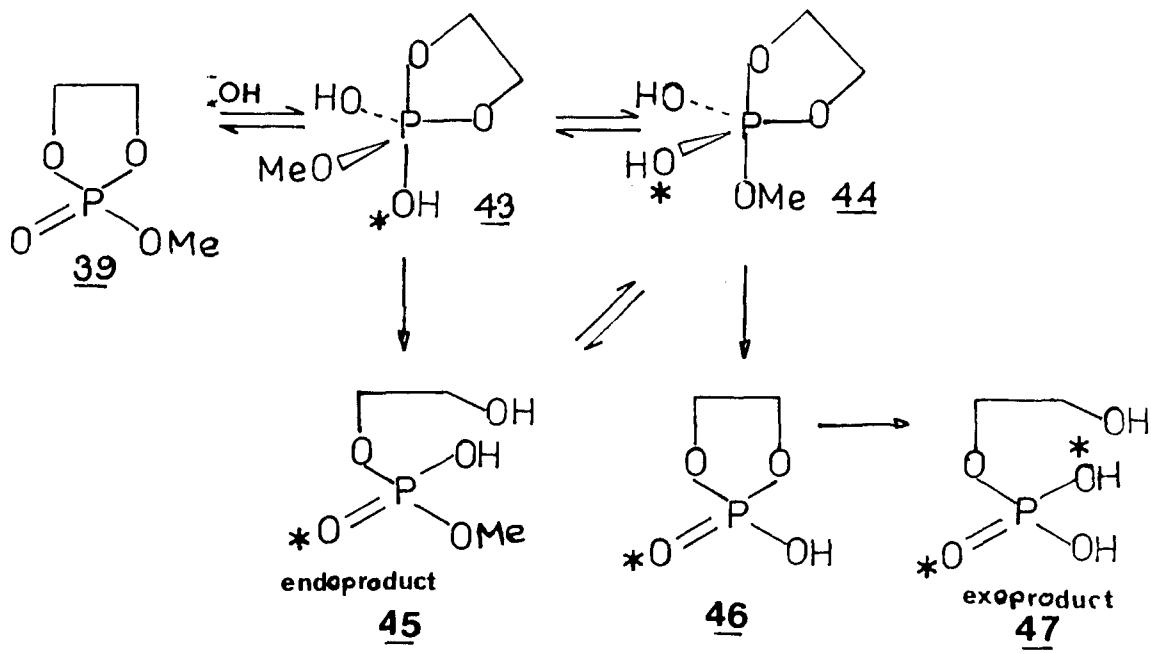


42

Westheimer and coworkers[39] proposed that this rate acceleration was due to relief of ring strain in the five-membered rings. Thermochemical measurements showed that ethylene phosphate 38 is indeed strained relative to the acyclic phosphate by ca 21-25 kJ/mol.[46] This strain

has been further confirmed by X-ray crystallography, on five-membered cyclic phosphate 40 .[47] The endocyclic O-P-O bond angle is 98.4°. However, it was demonstrated [38,39,46,48-50] later that the release of ring strain in forming a trigonal bipyramidal pentacovalent phosphorane transition state or intermediate was responsible for at most 16-25 kJ/mol of the 41-46 kJ/mol difference in activation energies between the base-catalyzed hydrolysis of methyl ethylene phosphate 39 and that of trimethyl phosphate. Recently Gorenstein and coworkers[52-54] proposed, based on molecular orbital calculations, that a significant fraction of this difference comes from orbital stereoelectronic effects in the trigonal bipyramidal transition state.

From O-18 labeling studies[52] it was concluded that the pathway for the formation of 47 was via 45 , 44 and 46. (scheme 4).

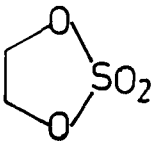


Scheme 4.
The hydrolysis pathway of methyl ethylene phosphate.

Gorenstein and coworkers believe that the dianionic form of 44 is formed via rapid pseudorotation[48] in base of 43 . The two lone pairs on the equatorial ring oxygens (assuming sp^3 hybridization[55]) are oriented partially antiperiplanar to the axial ring ester bond of the leaving group. Molecular orbital calculations suggested that this antiperiplanar lone pair orientation could facilitate P-O bond cleavage and that proper orbital overlap (the stereoelectronic effect) could be responsible for as much as a 46 kJ/mol lowering of the transition state

energy.[50,56,57] In the five-membered cyclic esters the ring constrains the lone pairs in a stereoelectronically favorable orientation while in the acyclic case, proper antiperiplanar lone pair overlap in the transition state would require freezing of one or more rotational degrees of freedom about the ester bonds.[57] It is significant that a considerable portion of the rate difference between cyclic and acyclic reaction is entropically driven.[57]

The initial attempt to find examples of reactivity comparable to the fived-membered cyclic phosphates in analogous sulfur compounds was carried out with the substrates ethylene sulfate 48 , trimethylene sulfate 49 and dimethyl sulfate 50 .[58]



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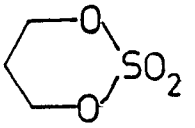

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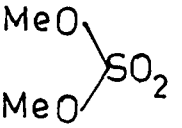


50

Ethylene sulfate 48 hydrolyzed in alkaline solution some twenty times faster than dimethyl sulfate 50 and approximately one hundred times faster than the six-membered analogue 49 . However; whilst ethylene sulfate hydrolyzed partially (14%) by sulfur-oxygen bond cleavage, 49 and 50 hydrolyzed exclusively with carbon-oxygen bond

cleavage, so that the relative rates of attack at sulfur in these systems could not be accurately determined. To overcome this problem, Kaiser and coworkers[59-61] synthesized compounds 51 - 56 (fig 5).

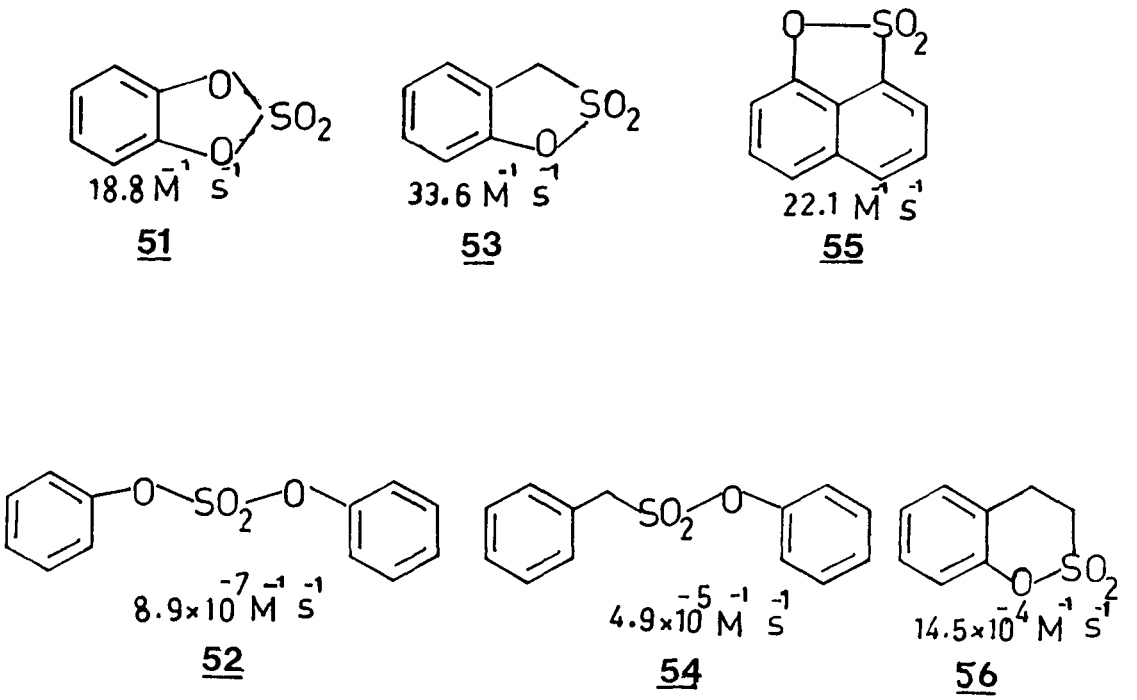


Figure 5.
Second order rate constants for the alkaline hydrolyses of sulfate esters and sultones.

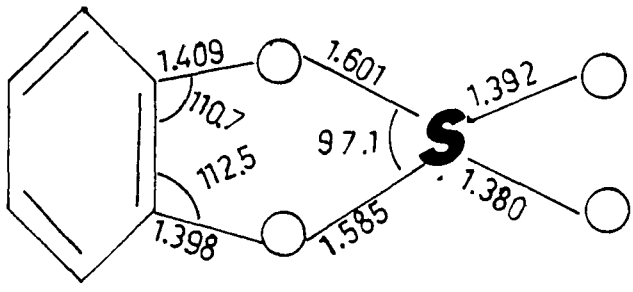
Analogous to the five-membered ring cyclic ester phosphates, the five-membered aromatic sulfate, o-phenylene sulfate (51), hydrolysed 2×10^{7} times faster than

diphenyl sulfate (52).[59] o-Hydroxytoluenesulfonic acid sultone (53) showed a rate $7x10^6$ faster than its open chain analog, phenyl p-toluenesulfonate (54).[60,61] Furthermore, the rate of hydrolysis of the six-membered cyclic sulfonate 56 is about 10^4 times less than that of 53 . This leads to the order of reactivity: five-membered ring >> six-membered ring > open chain analogue. [62] Thermochemical measurements show that the chief driving force for the rapid ring-opening of the five-membered heterocycles is ring strain. Thus, the heat of hydrolysis of ethylene sulfate is 21-25 kJ/mol more than for dimethyl sulfate.[58,63]

The strain in alicyclic systems has been discussed primarily in terms of bond angle deformations, bond stretching, torsion about the dihedral angles and nonbonding interaction.[64,65] Much of the discussion of the origin of ring strain in cyclic sulfate esters was centered around three possible causes: angle strain, strain-induced changes in 2p-3dπ -character of the endocyclic oxygen-hetero atom bonds,[66,67] and 1,3-nonbonding interactions between the oxygen atoms.[58]

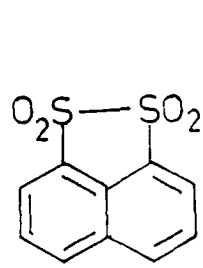
X-ray structural analysis showed the presence of ring-strain in five-membered cyclic sulfates and sultones. The internal O-S-O bond in sulfate 51 is only 97.1^{o}[67] and the corresponding C-S-O angle in sultone 53 is 96.1^{o}[68] The six-membered sultone 56 , which undergoes alkaline hydrolysis only ten times faster

than its open chain analogue, is much less strained than the five-membered ring. This sultone has a much larger internal C-S-O bond angle of 101.4° and a larger C-O-S bond angle of 116.9° compared to 108.9°[69] in the five-membered ring. Boer and Flynn[70] showed that all the angles in catechol sulfate (51), are strained. The O-C-C angles are distorted to values of 112.5° and 110.7°, well below the normal angle for sp^2-hybridized carbon of 120°. The two S-O-C angles (108.6° and 108.7°) are also considerably less than the values expected for an acyclic sulfate (120.6°). The internal O-S-O bond angle of 97.1° is substantially below the tetrahedral angle of 109.5°. The exocyclic S-O bond distances are 1.380×10^{-8}cm and 1.392×10^{-8}cm, the S-O bonds in the ring are 1.585 and 1.601×10^{-8}cm, and the C-O distances are 1.398 and 1.409×10^{-8}cm. The unexpected feature of the structure is the distortion of the five-membered ring to a nonplanar envelope structure where the sulfur atom lies 0.249×10^{-8}cm above the plane through the six carbon atoms and the two ring oxygen atoms.[70] This result suggests that lone pair repulsions may play a role in the extraordinarily high rate of alkaline hydrolysis exhibited by five-membered cyclic esters of sulfur and phosphorus as compared to their six-membered or acyclic analogues.



51

Incontrast to the sultone 55 which hydrolyses 2.5×10^7 times faster than its open chain analog,[60,61] the disulfone 57 does not hydrolyze significantly faster than either open chain phenyl disulfone or disulfone 59 . Kice[71] suggested that the lack of rate acceleration for the cyclic five-membered disulfone 57 compared to the six-membered sulfone 59 was due to either a lack of significant strain associated with the disulfone ring in 57 , or that there is no relief of strain upon going from reactant to transition state or intermediate as there is in the reaction of cyclic sulfates and sultones. It is possible that the intermediate or transition state 58 has eclipsing oxygens which hinder the reaction and decrease its rate.



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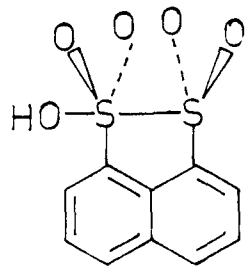

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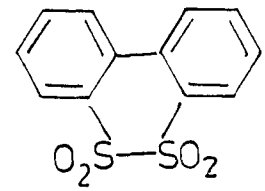
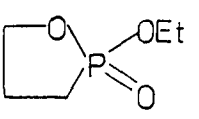
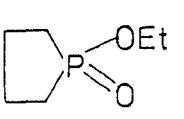
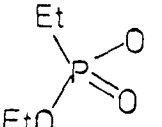


59

An earlier proposal that 2p-3dπ bonding between the endocyclic oxygen atoms and hetero atom could induce strain in cyclic phosphate esters has now been largely abandoned,[62] because ^{31}P nuclei in strained cyclic esters appear in the NMR to be less shielded than in unstrained compounds.[67] It was thought for a time that ring strain reduces 2p-3dπ bonding between phosphorus and oxygen.[58,66,67] However, ring strain created no difference in the exocyclic and endocyclic P-OC bond lengths,[72,73] so this effect was not corroborated by the experimental data.

There is another important factor which could cause the kinetic acceleration. Determination of the Arrhenius parameters for the alkaline hydrolyses of cyclic and open chain phosphoryl compounds showed that some of the high reactivity of five-membered cyclic phosphates arose from a more favorable entropy of activation[74] (table 1).

Table 1.
Rate constants and activation parameters for the alkaline hydrolyses of cyclic and open chain phospholan

	 **60**	 **61**	 **62**
rate($l\ mol^{-1}/s$)$\times 10^4$	5.4×10^5	1.18	1.72
E (kJ/mol)	48.9 ± 4.2	171.96 ± 2.0	58.6 ± 2.0
$\Delta S^{\ddagger}$	-69.5	-146.4	-143.1

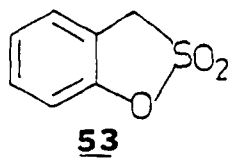
The greatest contribution to the 5×10^5 rate difference between phospholan 61 or acyclic oxaphospholan 62 and the cyclic oxaphospholan 60 comes from the more favorable activation entropy of the latter ester.[74]

Tillett and coworkers[75] measured the relative reactivity of alkaline hydrolyses of sulfonate esters 53 , 54 , 56 , 63 , and 64 (table 2). They concluded that the differences in reactivity between the five-membered sultone 53 and the other sulfonate esters arose from a combination of both enthalpy and entropy strain. As the ring size decreases from seven to five, the entropy of activation becomes more favorable. In terms of the "entropy-strain"

principle:[76] the molecule takes up a more ordered structure in the transition state for hydrolysis and so the molecular motions of the six-and seven-membered and open chain sulfonates are suppressed. This loss of entropy increases the free energy of activation. For the relatively reactive five-membered sultone 53 , the molecule is already constrained and there is a relatively small loss of entropy in reaching the transition state; hence, 55 has the smallest negative entropy of activation resulting in a lower free energy of activation. It is worth mentioning

It is worth mentioning that evidence for the E1cB mechanism of hydrolysis[76] of phenyl phenylmethane sulfonate 54 shows up clearoGly in the value of the entropy of activation, $\Delta S^{\ddagger}$ + 2.9 $JK^{-1}mol^{-1}$ (30^{o}), which is dramatically different from that of any of the other sulfonates studied[75].

Table 2.
Arrhenius parameters and relative rates of the alkaline hydrolyses of sulfonate esters



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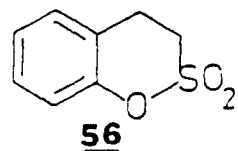

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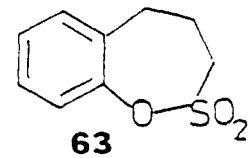
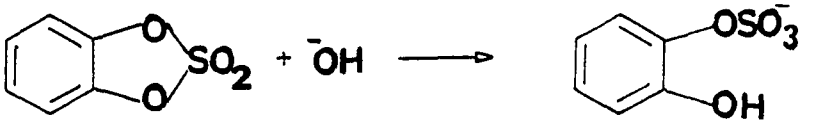


63

$PhCH_2-SO_2-OPh$ **54** $Ph-SO_2-OPh$ **64**

Sulfonate	k_{rel}	$\Delta H^{\neq}$/kJmol^{-1}	$\Delta S^{\neq}$/J K^{-1}mol^{-1}
53	110	45.3 ± 0.8	-61.2 ± 2.9
53	106	43.6 ± 0.8	-67.0 ± 2.1
56	5.2×10^{-3}	67.0 ± 1.3	-72.5 ± 4.3
63	5.1×10^{-5}	74.2 ± 1.3	-90.1 ± 3.8
54	3.9×10^{-4}	98.0 ± 2.6	+2.98 ± 4.2
64	1.0×10^{-3}	72.5 ± 0.4	-71.2 ± 2.1

By using oxygen-18 tracer techniques,[77,78] it was shown that alkaline hydrolysis of aryl sulfonates involved nucleophilic attack at sulfur with consequent sulfur-oxygen bond cleavage. From kinetic studies[48,73,76] the alkaline hydrolyses of both cyclic and open chain aryl sulfonates were shown to follow second-order kinetics, consistent with the overall reaction shown in eqs (5) and (6).



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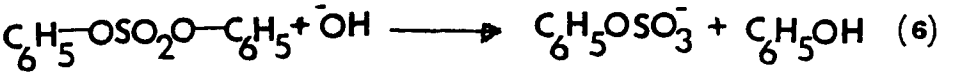
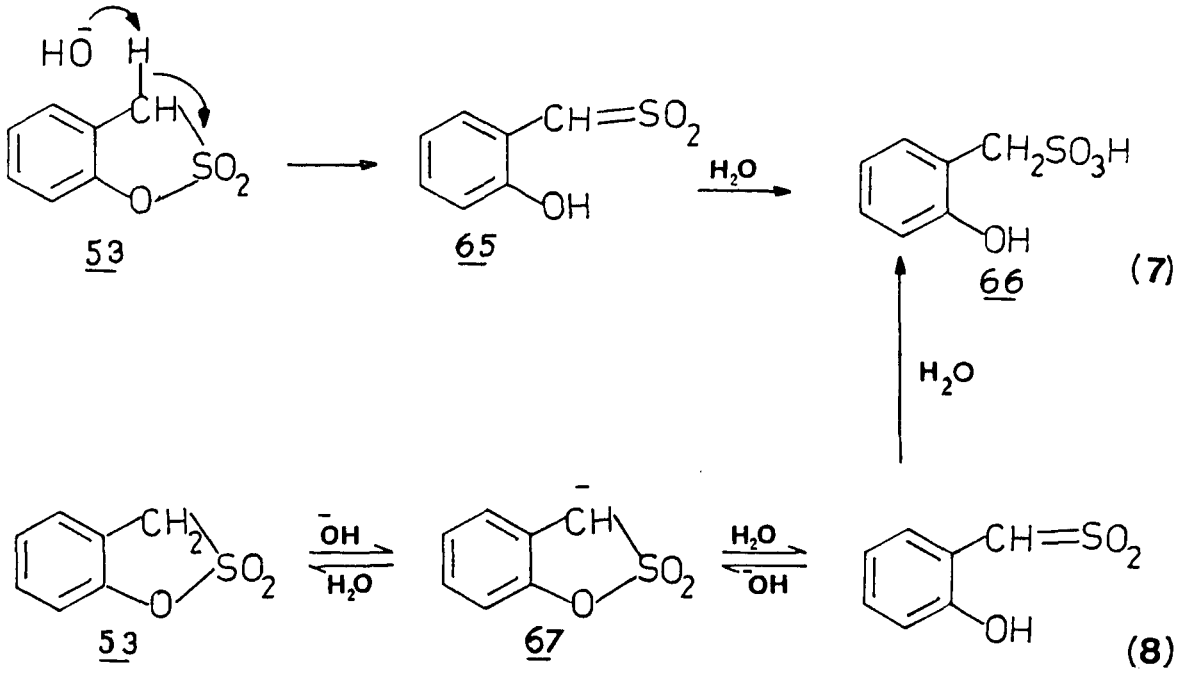


(6)

The kinetic and bond-fission studies suggest that the hydrolysis of phenyl arenesulfonates proceeds via nucleophilic attack of hydroxide ion at sulfur. For the cyclic sulfonates 53 , 56 , 63 and the open chain sulfonate 54 , other mechanisms are possible[75] which involve the formation of carbanions and/or sulfenes as intermediates (scheme 5).



Scheme 5.
Sulfene pathways for the alkaline hydrolyses of sultones.

The mechanism shown in equation 7 was eliminated by Kaiser and coworkers[79] who ran the reaction in D_2O. If the reaction were concerted, or irreversible, the resultant sulfonic acid 66 should have one deuterium atom incorporated into the methylene group, but no deuterium was found in the product. When the hydrolysis of 53 was conducted in a D_2O-OD^- solution in which the sultone was in excess over the OD^-, sultone 53, recovered after all the OD^- was consumed, was found to have undergone extensive exchange of deuterium onto the

methylene group. This observation indicated that carbanion 67 was formed rapidly and reversibly from sultone 53 in basic solution (eq 8). This leaves open the question whether or not a carbanion and/or sulfene intermediate is on the reaction pathway for the alkaline hydrolysis of sultone 53 . Kaiser[63] concluded that a carbanion-sulfene mechanism as in eq 8 does not provide an important pathway for the hydrolysis of the five-membered sultone, since the rate of hydrolysis of this compound is much faster than for the open chain sulfonate.

Later williams and coworkers[80,81] showed that the hydrolysis and aminolysis of phenyl phenylmethanesulfonate proceeds via a stepwise elimination-addition mechanism (E1cB) involving a sulfene intermediate (scheme 6).

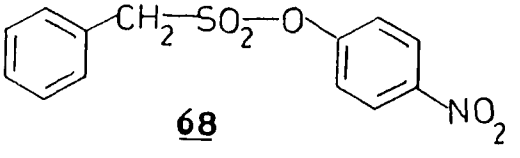
$$PhCH_2SO_2OAr + B \rightleftharpoons PhC\bar{H}SO_2OAr + BH^+$$

$$PhC\bar{H}SO_2OAr \rightarrow PhCH{=}SO_2 + ArO^-$$

$$PhCH{=}SO_2 + H_2O + B \rightarrow PhCH_2SO_3^- + BH + H^+$$

Scheme 6.
Elimination-addition mechanism of aminolysis of phenyl phenylmethanesulfonate.

Evidence for the formation of a sulfene intermediate via an E1cB mechanism has also been reported by King and Beatson.[82] They found that some sulfonates reacted with triethylamine in DME and D_2O by either a reversible or an irreversible E1cB process depending on the leaving group. If p-nitrophenyl phenylmethanesulfonate 68 was the substrate, deuterated 69 and 70 were obtained which suggests that the mechanism of the reaction is a reversible E1cB. If 71 was the substrate, the sulfonate recovered after partial reaction was unexchanged so an irreversible E1cB mechanism was being followed here. The formation of monodeuteriated 72 also suggested the formation of sulfene in the reaction pathway.



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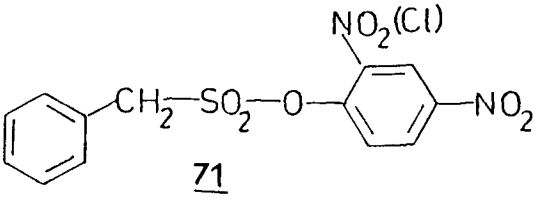

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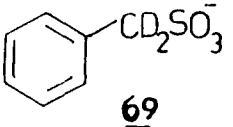

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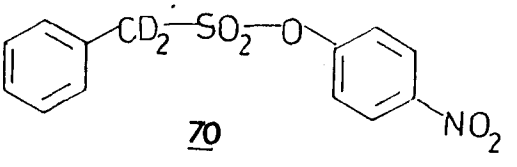

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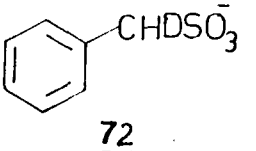
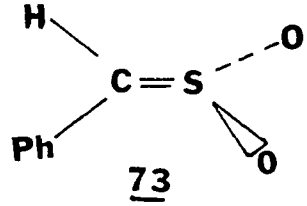


72

Williams[81] also proposed that for the five-membered cyclic sulfonate 53 , although the benzylic proton is labile and the phenoxide ion is a good leaving

group, the E1cB mechanism is suppressed because the transition state for this reaction can only lead to the high energy sulfene 73 in which the OSO plane is perpendicular to HC_2S plane.



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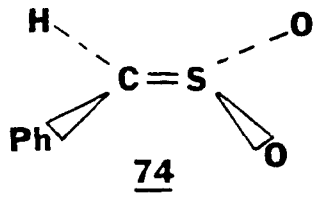
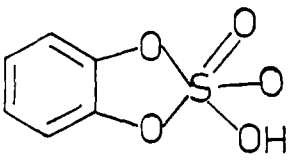


74

The planar sulfene 74 is calculated to be more stable by some 147 kJ/mol than the perpendicular form 73 .[80] It is not likly that the sulfene pathway is followed for the alkaline hydrolysis of sultone 53 .

An alternative mechanism for the alkaline hydrolysis of cyclic sulfates is a stepwise S_N2 type mechanism.[62] By analogy with substitution reactions at phosphorus, it seems reasonable to assume that a pentacoordinate intermediate of type 75 would be formed and that strain would be relieved if such an intermediate had a trigonal bipyramidal structure (76).



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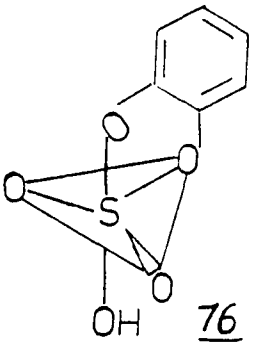
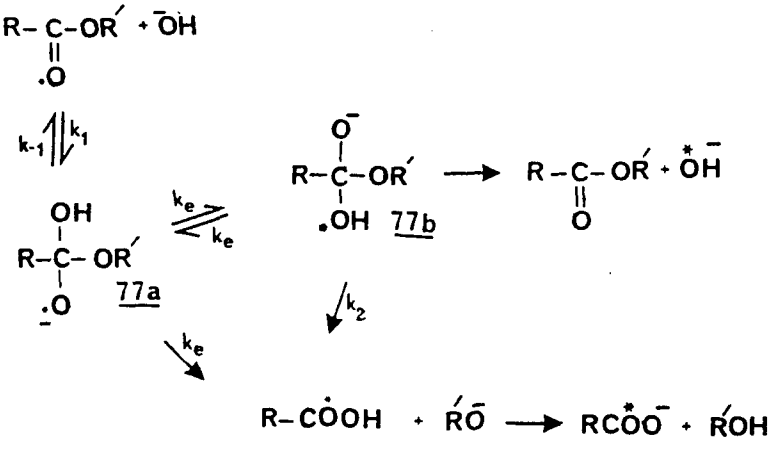


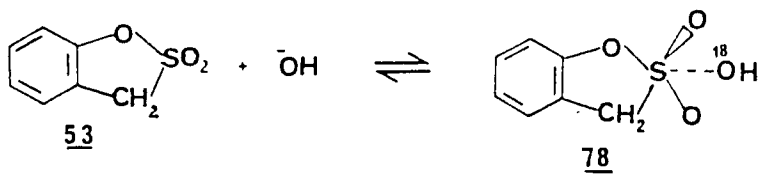
76

The classic method for demonstrating the presence of an intermediate such as 77 on the reaction coordinate in the hydrolysis of a carboxylic ester is by using O-exchange. Bender[83] showed that in the alkaline hydrolysis of RC(O-18)OR' the ester recovered after partial hydrolysis had undergone substantial loss of oxygen-18 label (scheme 7).

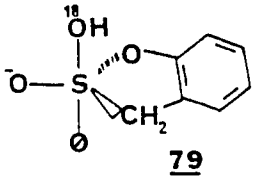


Scheme 7.
Hydrolysis of carboxylic ester (O-18).

Attemps to detect the presence of trigonal bipyramidal intermediates in nucleophilic substitution reactions at sulfur by oxygen-18 exchange have not been successful. No oxygen exchange could be detected in the unhydrolysed sulfonate recovered after partial hydrolysis in alkaline solution of either phenyl p-toluenesulfonate,[72,82,84,86] N-mesitylarenesulfinamide,[87] 2-hydroxytoluenesulfonic acid sultone (53) or 2-hydroxyphenylethane sulfonic acid sultone (56).[85] However, the absence of oxygen exchange does not rule out the possibile formation of a pentacoordinate intermediate.[88,89] Bender[83] originally pointed out that the lack of back exchange does not rule out the existence of an intermediate. If the rate of oxygen equilibration of an intermediate were much slower than its rate of decomposition, no oxygen exchange would be observed. If a trigonal bipyramidal intermediate 78 was formed in the hydrolysis of sulfonate 53 in labeled aqueous base (eq 9), pseudorotation of 78 would lead to the trigonal bipyramidal intermediates shown in fig 6. Their enantiomers, which are also possible, are not shown.



53 78 (9)



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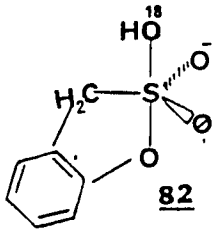

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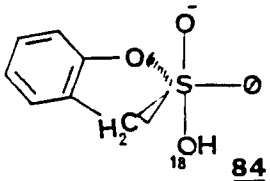

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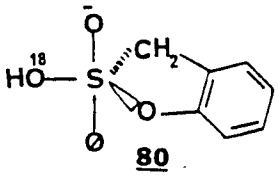

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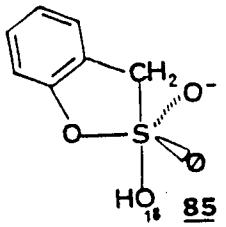

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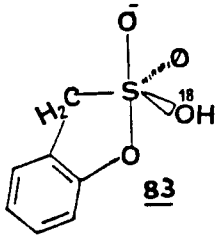

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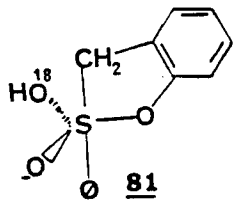

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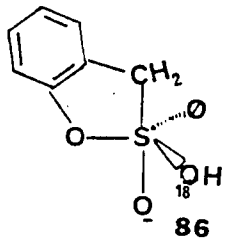
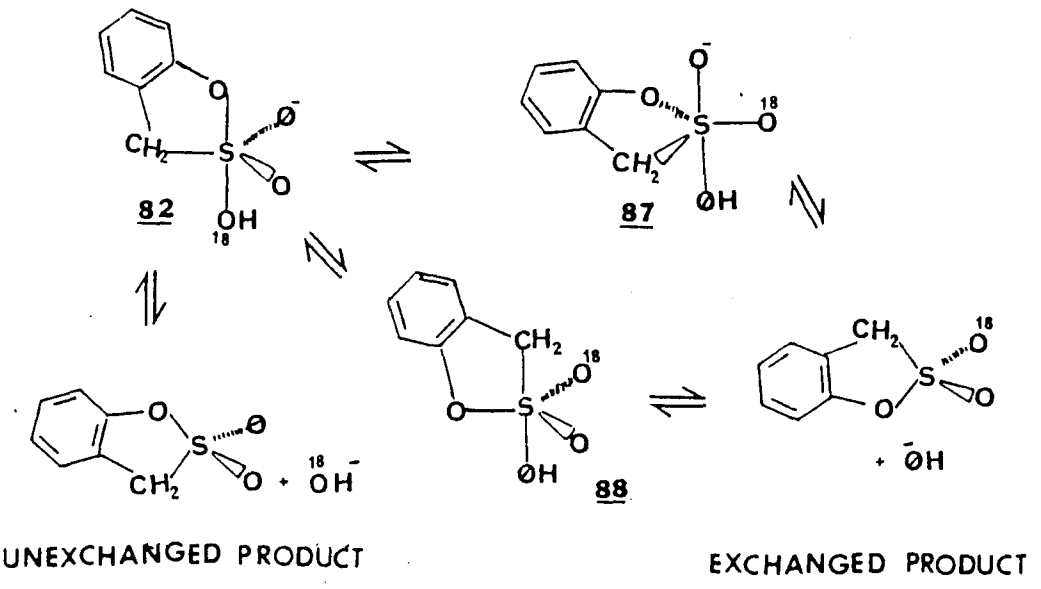


86

Figure 6.
Pseudorotation of trigonal bipyramidal intermediates.

Kaiser and Kézdy[8] pointed out that the failure to observe oxygen exchange in the hydrolysis of sultones can be predicted if the preference rule which applies to pseudorotation of the intermediate in phosphate ester hydrolysis can be applied to the pentacoordinate sulfur intermediate. Thus 79 , 80 and 84 which have ring atoms in equatorial positions would be undesirable intermediates because of the 120° ring angles. The apical positions of the methylene group of 81 , 85 and 86 make these intermediates unfavorable. Since negatively charged groups would be expected to occupy equatorial positions,[75] equilibration of the oxygen atoms in intermediate 82 with those in 87 and 88 (scheme 8) by pseudorotation and proton transfer is not likely to be involved in the mechanism of hydrolysis of sultone 53 . Intermediate 82 cannot undergo pseudorotation to 87 which would expand the ring angle to 120°, whereas pseudorotation about O would put the ring methylene group into an unfavorable apical position. The situation is similar to that observed for the methyl ester of propyl phosphoric acid[38] and for the hydrolysis of a cyclic sulfinate.[90]



Scheme 8.
Pseudorotation of trigonal bipyramidal intermediates leading to oxygen exchange.

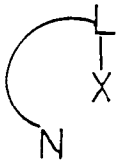
In order to compare the reactivity of 3-tosyl-1,2,3-benzoxathiazole-2,2-dioxide with aqueous base to the analogous published reactivities of acyclic and cyclic sulfate and sulfonate esters, a kinetic study of the cyclic sulfamate's hydrolysis in alkaline aqueous acetonitrile was undertaken. In addition, its reactions with various nucleophiles was investigated.

RESULTS AND DISCUSSION

PART I

Investigation of Endocyclic Nucleophilic Substitution at Di- and Tetra-coordinate Sulfur

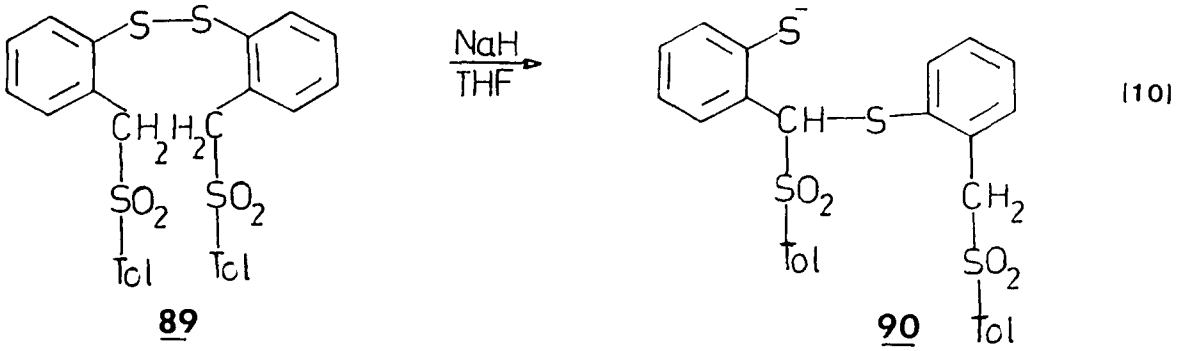
The aim of this research was to investigate endocyclic nucleophilic substitution at di- and tetra-coordinate sulfur. Molecules which appeared capable of undergoing endocyclic nucleoplilic substitution were synthesized for this purpose and their base-induced rearrangements attempted. The sulfur group of the substrate molecules were restricted to -S- or $-SO_2-$, the nucleophilic atoms were C or N, and the leaving atoms N, O or S. The ring sizes involved in the intermediates or transition states were limited to four-, five- and six-membered rings.



$X = -S-, -SO_2$
$N = C, N$
$L = N, O, S$

Because little is known about nucleopnilic substitution at dicoordinate sulfur(II), and a symmetrical

disulfide is easy to synthesize, bis-2-(4-toluenesulfonyl) methylphenyl disulfide (89), was prepared by known methods.[1] It was hoped that upon treatment of disulfide 89 with sodium hydride in THF, an endocyclic rearrangement to 90 would occur (eq 10).



89 90 (10)

Upon workup of the reaction mixture, 90 was not isolated, but rather sodium 4-toluenesulfinate (31.2%) and a white solid, melting point 213-214 °C, were obtained. This latter compound contained 67.85 per cent carbon and 3.40 per cent hydrogen (atomic ratio ca. C:H = 7:4), and had an apparent molecular ion at m/z 240 (100%), an M+1 ion at 241 (16.7%) and an M+2 ion at 242 (10.0%). Only aromatic protons were observed in the ^{1}H NMR and only six peaks in the ^{13}C NMR indicating that the molecule was symmetrical. Four bands were observed in the IR: two of medium intensity at 1432 and 1330 cm^{-1} and two strong

bands at 736 and 710. A sodium fusion test showed that the molecule contained sulfur. The compound was identified as [1]benzothieno[3,2-b][1]benzothiophene (91 , scheme 9). Mention of the reaction of aryl disulfides with sodium hydride was not found in the literature. However with n-butyllithium the reaction of diphenyl disulfide gives metalation products as well as n-butyl phenyl sulfide which could arise from nucleophilic attack at sulfur [91] (eq 11).

$$\mathrm{Ph{-}S{-}S{-}Ph} \xrightarrow{\text{n-BuLi}} \begin{array}{l} \mathrm{n\text{-}Bu{-}S{-}Ph}\ (31.4\%) \\ + \\ \mathrm{LiPh{-}S{-}S{-}PhLi}\ (43\%) \\ + \\ \mathrm{Ph{-}S{-}S{-}Ph}\ (17.9\%) \\ + \\ \mathrm{BuH} \end{array} \qquad [11]$$

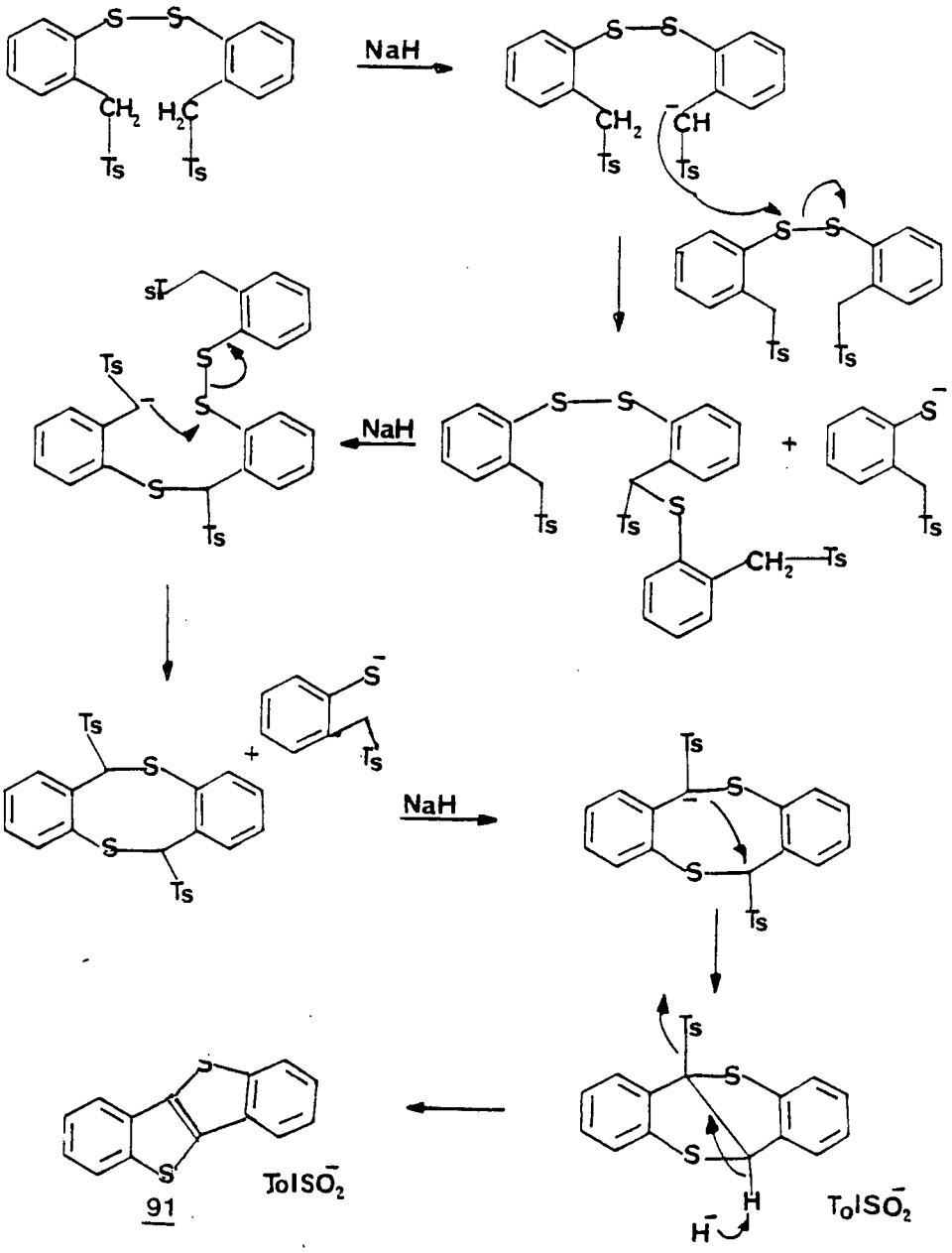
It is believed that the scission of the -S-S- bond by nucleophiles is of the S_N2 type.[92]

$$\mathrm{R{-}S{-}S{-}R^2} + \mathrm{Nu} \rightleftharpoons \mathrm{R{-}S{-}Nu} + \mathrm{R^2S^-} \qquad [12]$$

Miotti and coworkers[93] concluded from studies of the alkaline cleavage of disulfides that several mechanisms are

operative depending on the structural features of the substrates. Thus, the concurrent operation of more than one mechanism in the same system should not be excluded. A difficulty in deciding which mechanism is operative in the cleavage of disulfides is that the initial products (intermediates) are not easily isolated and identified. The final products can conceivably be accounted for by more than one mechanism.

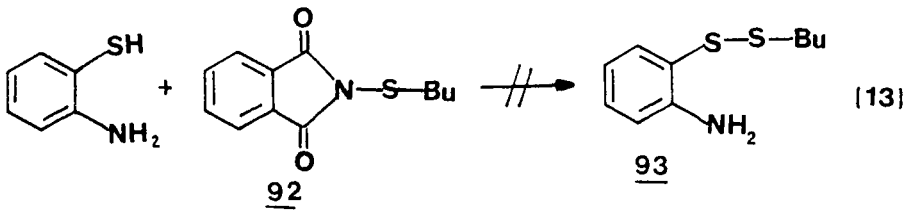
For disulfide 89 , both the $-SO_2-$ of the tosyl group and the -S-S-function are susceptible to hydride attack. There is also the possibility of deprotonating the methylene group. Thus, the reaction may follow more than one mechanism. Scheme 9 is the proposed mechanism for forming 91 from the reaction of 89 with sodium hydride.



Scheme 9.
Proposed pathway for the formation of 91 .

Since compound 91 was apparently not produced by endocyclic substitution, this reaction was not investigated further. But one more disulfide which has no tosyl group was synthesized.

An attempt to prepare the desired unsymmetrical disulfide 93 was made by the reaction of N-butyl thiophthalimide 92 with 2-aminothiophenol[94,95] (eq 13).



92 93 (13)

Instead of compound 93 , the symmetrical disulfide 94 was obtained. It is possible that the o-aminothiophenol was air oxidized to disulfide 94 , or that the unsymmetrical disulfide 93 was formed first followed by attack by another molecule of 2-aminothiophenol to form disulfide 94 . When disulfide 94 was treated with sodium hydride (eq 14), only starting material was obtained.

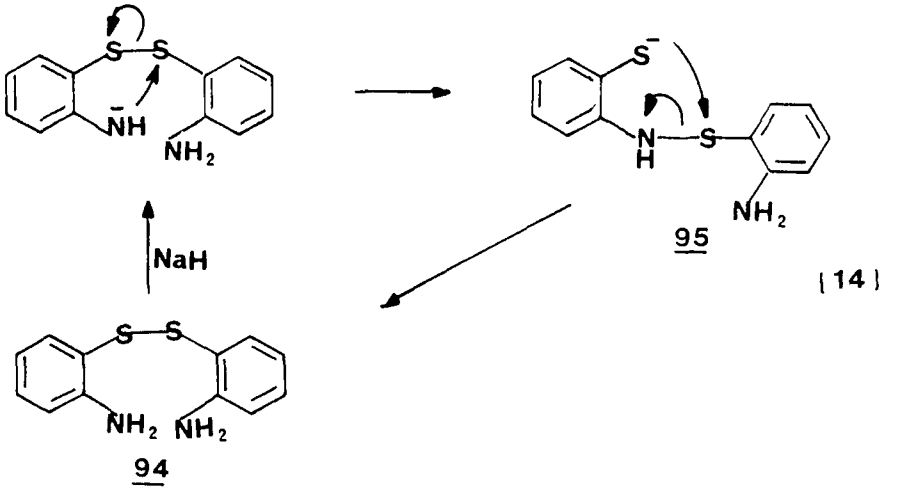
Since amino nitrogen is a poor nucleophile at sulfur, whereas sulfur is one of the best (fig 7),[96] there are at least two explanations for this result: (1) no reaction at sulfur took place or (2) the product 95 was formed and the better sulfur nucleophile, $-S^-$, attacked at the

sulfenamide sulfur of the same or another identical molecule resulting in the formation of the starting material[92] (eq 14).

$$(C_2H_5O)_3P > R^-, HS^- > C_2H_5S^- > C_6H_5S^- > (C_6H_5)_3P > SO_3^= >$$

$$OH^- > 2,4\text{-}(NO_2)_2C_6H_3S^- > N_3^- > SCN^-, I^-, C_6H_5NH_2$$

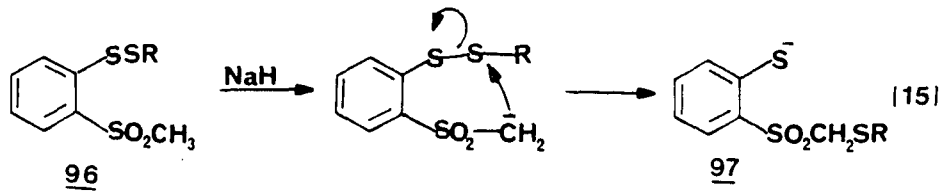
Figure 7.
Nucleophilicity toward sulfur.



(14)

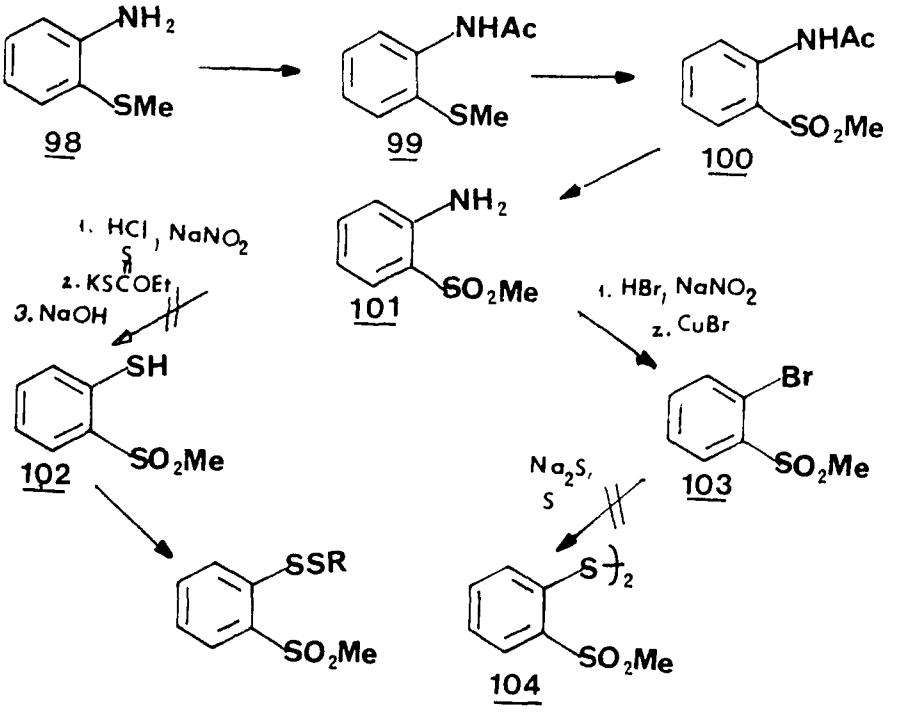
Pryor's[96] sulfur nucleoplilicity list shows that a carbanion is higher in nucleophilicity than mercaptide ion. Therefore, an attempt was made to synthesize disulfide 96 . With strong base, disulfide 96 should form a carbanion at the methyl group. A consequent rearrangement of this

compound would involve a six-membered transition state or intermediate (eq 15).



96 97 [15]

The starting material, 2-aminothiophenol was methylated[97] to form 2-aminophenyl methyl sulfide, 98 . Then the amino group of sulfide 98 was protected as an acetanilide[98] before the sulfide was oxidised to the sulfone.[99] Deprotection of the amino group was done by refluxing the sulfone in aqueous sodium hydroxide (scheme 10).

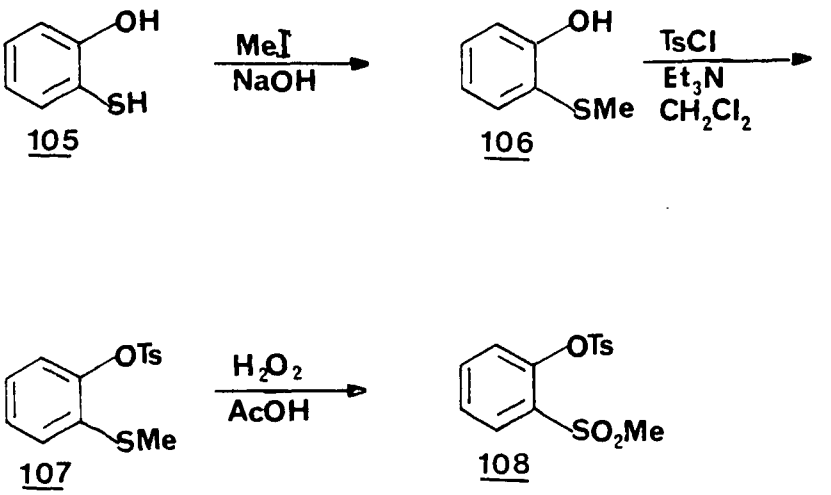


Scheme 10.
The synthesis of 2-aminophenyl methyl sulfone.

Attempts to convert sulfone 101 to 2-mercapto phenyl methyl sulfone (102)[100] or disulfide 104 [101] were unsuccessful.

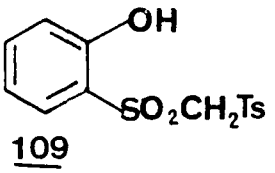
Further investigation of endocyclic nucleophilic substitution at tetracoordinate sulfur was carried out on 2-(methylsulfonylphenyl) 4-toluenesulfonate, 108 . The starting material, 2-mercaptophenol (105) was prepared by

known methods from o-aminophenol.[102] Then the next steps of the synthesis were carried out as shown in scheme 11.[97,99,103]



Scheme 11.
The synthesis of 2'-(methylsulfonyl)phenyl 4-toluenesulfonate.

Sulfonate 108 was treated with sodium hydride but no rearranged product, 109 , was isolated. Instead 2-hydroxyphenyl methyl sulfone (110) (74.9% yield) starting material (2.46%) and sodium 4-toluenesulfonate were isolated.



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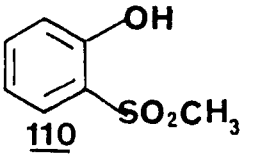

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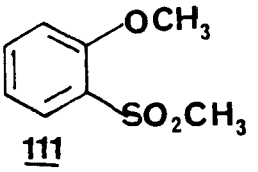

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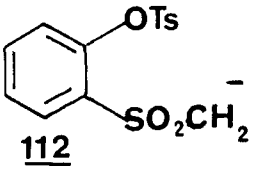
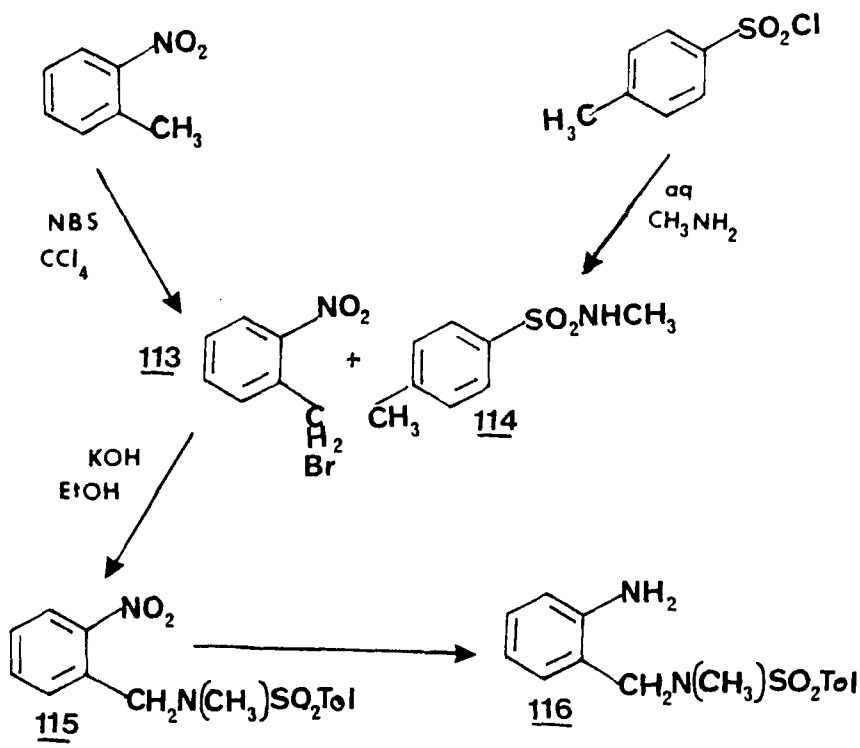


112

In this reaction it appears that the hydride ion reacted as a nucleophile and attacked the sulfur of the tosyl group to form 4-toluenesulfinate anion. Somehow this sulfinate was oxidized to the sulfonate.[104] Attempts to trap anion 112 by quenching the reaction mixture with methyl iodide were unsuccessful; only the oxygen methylated sulfone 111 was found along with the 4-toluene sulfonic acid. Sulfonate 108 was also reacted with LDA; only the starting material was recovered. Since no color change occurred in the reaction mixture and no carbanion 112 was trapped by methyl iodide, we assume that no anion was formed.

N-methyl-N-(2-aminobenzyl)-4-toluenesulfonamide (116) was synthesized as shown in scheme 12. Bromination of 2-nitrotoluene with N-bromosuccinamide[105,106] gave 2-nitrobenzyl bromide which was then treated with N-methyl 4-toluenesulfonamide in the presence of potassium hydroxide

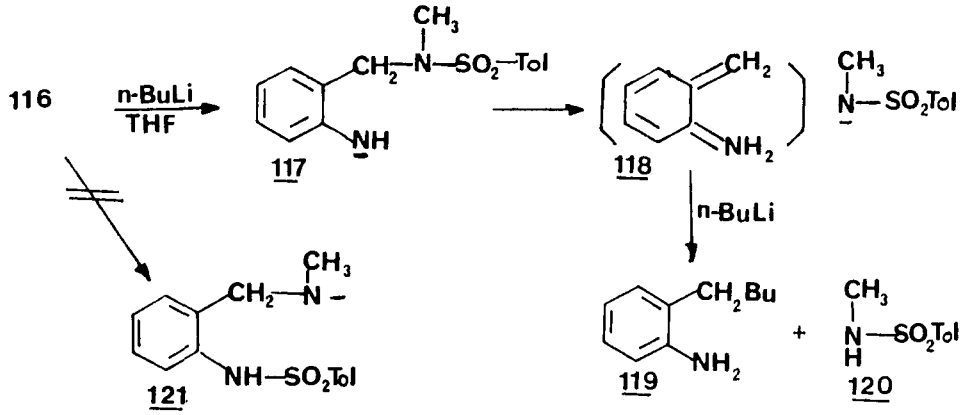
to form N-methyl-N-(2'-nitrobenzyl)-4-toluenesulfon amide.[107] N-methyl 4-toluenesulfonamide was synthesized from methylamine and 4-toluenesulfonyl chloride.[108]



Scheme 12.
Synthesis of N-methyl-N-(2'-aminobenzyl) 4-toluenesulfonamide.

Nitrosulfonamide 115 was reduced to the aminosulfonamide 116 using tin and 10% hydrochloric acid in 50% yield.[109] A better yield (80%) was obtained using stannous chloride and a small amount of concentrated hydrochloric acid. Sulfonamide 116 was treated with

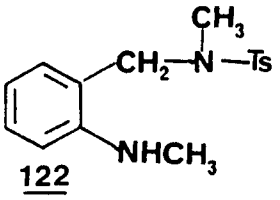
n-butyllithium (3-4 equivalents) in THF at 0°. A bright red-orange color appeared after 20 minutes. Upon workup, 6 spots were observed on TLC. By chromatography on preparative silica plates, two compounds were isolated: 2-pentyl aniline (119) in 15-20 per cent yield and N-methyl 4-toluenesulfonamide (120) in 25 per cent yield. No trace of rearrangement product 121 was found. The two isolated products suggest that an elimination-addition mechanism is being followed for at least part of the reaction (scheme 13).



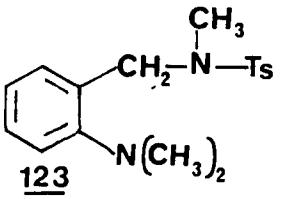
Scheme 13.
The pathway of elimination-addition of N-methyl-N-(2'-aminobenzyl)-4-toluenesulfonamide.

Anion 117 was formed[110] by n-BuLi deprotonation of the amino group followed by 1,4-elimination with consequent

formation of 118 and N-methyl 4-toluenesulfonamide anion. n-butyllithium then added to 118 to give 119 . Trapping of anion 117 was done by adding methyl iodide to the reaction mixture as soon as the bright red color appeared. N-Substituted sulfonamide 122 and 123 were isolated.

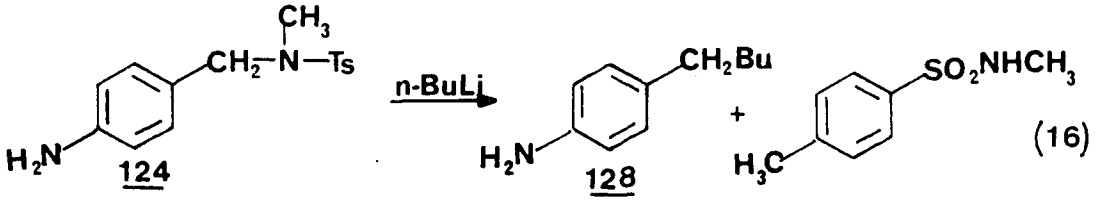


122

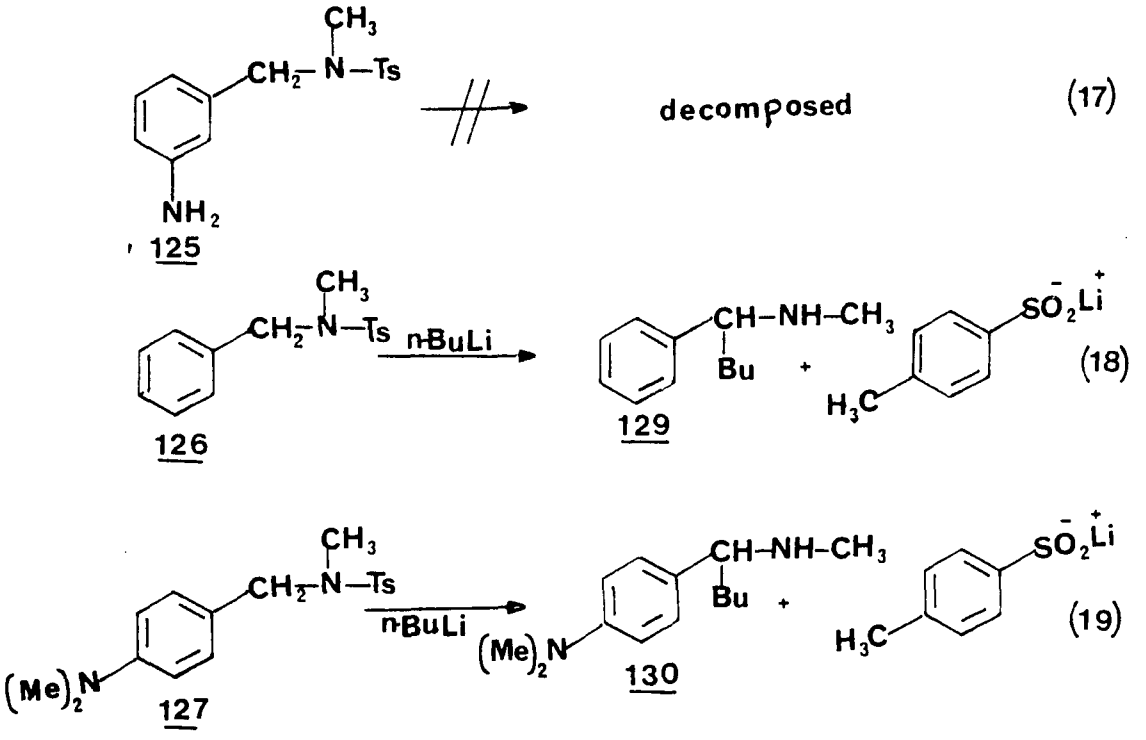


123

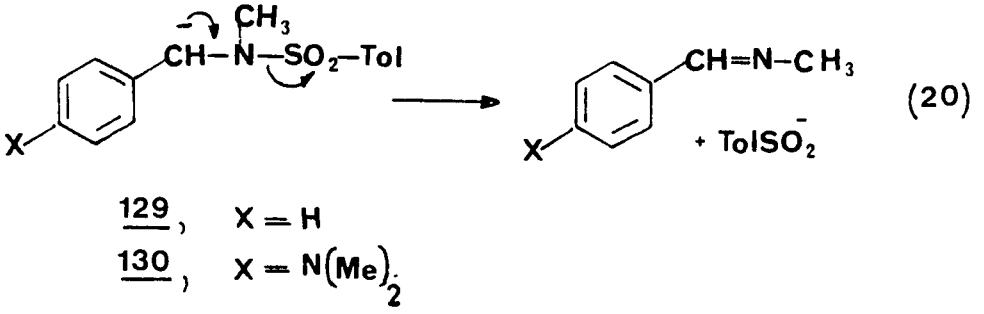
The elimination-addition reaction of sulfonamide 116 was quite interesting, so we investigated it further by synthesizing sulfonamides 124 - 127 and then treating them with n-BuLi (eq 16-19).



124 128 (16)



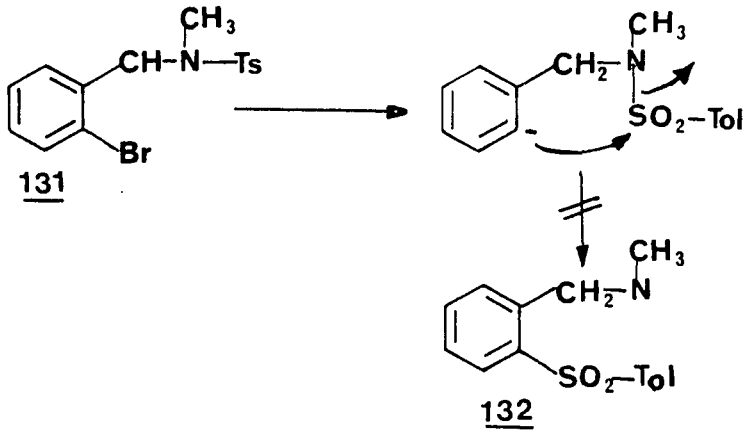
Sulfonamide 124 reacted in the same way as did sulfonamide 116 (eq 26) except by 1,6- rather than 1,4-elimination. Then addition occurred to give N-methyl 4-toluenesulfonamide and 4-pentylaniline 128 . Reaction of 126 and 127 with n-BuLi took a different course. The tosyl group was eliminated by β-elimination and N-S bond cleavage occurred as shown by eq 20. Compounds 129 and 130 were formed by addition of n-BuLi to the corresponding imines. In both cases, attempts to trap the imines with thiophenol were unsuccessful.



(20)

129, X = H
130, X = N(Me)2

Sulfonamide 131 was synthesized; when it was treated with n-BuLi no trace of the hoped-for rearrangement product 132 was detected (TLC and crude ^{1}H NMR). No further workup of the reaction mixture was attempted (eq 21).



(21)

The disulfides prepared for investigation were not good model compounds for the study of endocyclic nucleophilic substitution at dicoordinate sulfur(II). Upon treatment with base to create an anionic nucleophilic center, reaction products were formed whose origins were not readily attributable to endocyclic nucleophilic substitution processes.

In order to study endocyclic nucleophilic substitution at tetra-coordinate sulfur(VI), 2'-(methylsulfonylphenyl) 4-toluenesulfonate (108) and N-methyl-N-(2'-aminobenzyl)-4-toluenesulfonamide (116), both of which appeared capable of undergoing endocyclic nucleophilic substitution *via* cyclic six-membered transition states or intermediates, were prepared. Neither produced the hoped-for rearrangement products upon treatment with base, but gave rise to products having their origin in elimination. Perhaps the desired intramolecular reaction did not occur because proper alignment of the nucleophile with the sulfur atom could not be attained or the transition state or intermediate was of high energy. Even though sulfur does form isolable sulfuranes, and presumably short lived non-isolable sulfuranes as well, there are no reports of a stable species, formally arising from tetracoordinate sulfur(VI), which has the sulfur atom incorporated into a six-membered ring. Stable sulfuranes having five-membered rings spanning apical and equatorial positions are known.

Reactions which appear to be examples of endocyclic nucleophilic substitution at tetracoordinate sulfur(VI) are found in the work of Closson[34] and Hellwinkel.[35,36] They independently observed that the arenesulfonyl group of an N-aryl arenesulfonamide migrated intramolecularly from the nitrogen atom to a position ortho to the nitrogen of the aryl ring when the sulfonamide was treated with organolithiums, bases which created a nucleophilic site at the migration terminus. Presumably, this rearrangement, which is quite general, proceeds via a four-centered cyclic intermediate or transition state. Andersen[37] observed that 2-aminoaryl arenesulfonates rearranged intramolecularly to N-(2-hydroxyaryl) arenesulfonamides by migration of the sulfonyl group from oxygen to nitrogen when these esters were treated with lithium bases. But these reactions may actually proceed <u>via</u> an elimination-addition pathway rather than through the desired five-membered cyclic transition states or intermediates and so not be examples of endocyclic nucleophilic substitution.

A readily apparent explanation is not forthcoming to account for the difference in reaction pathways between those which follow and those which do not follow the endocyclic pathway. Perhaps a four-membered ring is better accomodated or more readily achieved in the apical and equatorial positions of a trigonal bipyramid, the geometry of the presumed sulfurane intermediate or transitiom state,

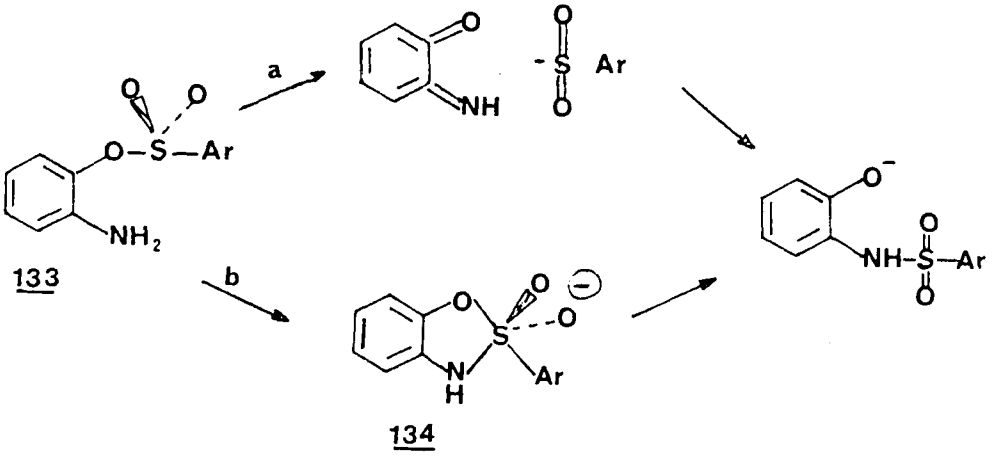
than are five- or six-membered rings. Yet, it should be remembered that in one of Hellwinkel's examples, the intermediate sulfurane has two rings, one five- and one four-membered. In analogous phosphorus chemistry,[135] a five-membered ring has been postulated as an intermediate in a possible case of endocyclic substitution. Therefore, it may simply be, and this seems more likely, that in the five- and six-membered cases, pathways lower in activation energy than the substitution process exist; e.g., elimination pathways, whereas in the four-membered cases they do not. Consequently, substitution is observed in the latter, and elimination in the former.

Further work in this area will be described in the Ph.D. thesis of Debra MacIntyre-Zoller.

PART II

Synthesis of 3-Tosyl-1,2,3-Benzoxathiazole-2,2-Dioxide and Its Reactions with Nucleophiles

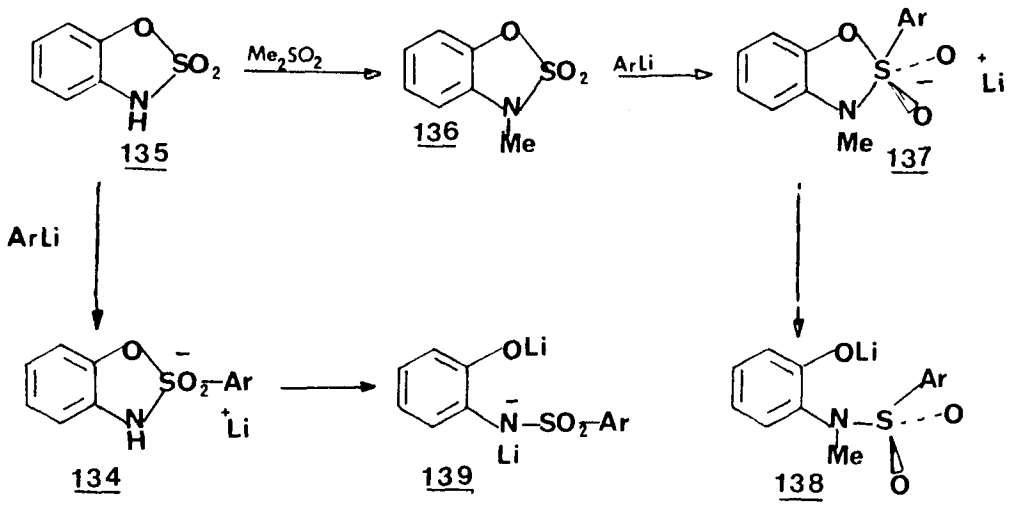
In the previous study of the rearrangement of 2-aminoaryl arenesulfonates to N-(2-hydroxyaryl) arenesulfonamides,[37] two mechanisms were proposed: elimination-addition (a), and endocyclic nucleophilic substitution (b) (scheme 14).



Scheme 14.
Proposed mechanisms for the rearrangement of 2-aminoaryl arenesulfonates.

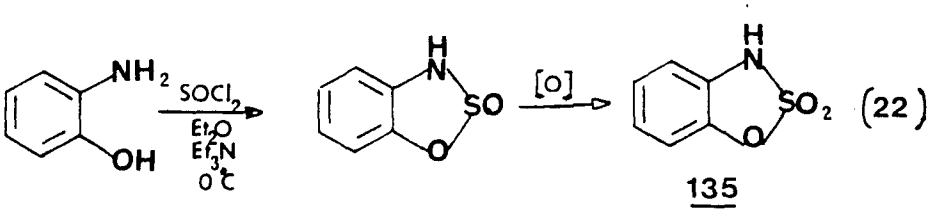
If path b were being followed, a cyclic intermediate or transition state[3] 134 would be expected. It was

suggested by a referee that the cyclic sulfamate 135 could be synthesized and then treated with phenyllithium to give 134 which would probably be unstable and give rise to 139 (scheme 15). We felt it would be desirable to remove the acidic hydrogen of 135 by methylation at the nitrogen to give 136 . If 136 gave 138 on reaction with an aryllithium reagent, this would provide support for the endocyclic pathway b for the rearrangement outlined in scheme 14.



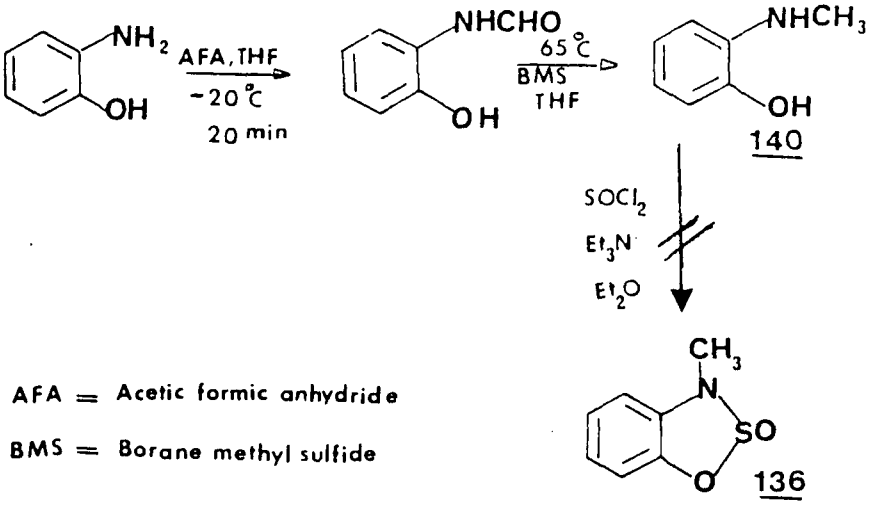
Scheme 15.
The proposed synthesis of the hypothetical intermediate in the rearrangement of 2-aminoaryl arenesulfonates.

In the first attempted synthesis of cyclic sulfamate 135 , o-aminophenol was treated with thionyl chloride (eq 22). The reaction mixture turned black after twenty minutes. Changing the temperature to -78° or to room temperature, using hexane or dichloromethane as solvent, and substituting sulfuryl chloride for thionyl chloride all resulted in black reaction mixtures. The reaction was followed by TLC. The major spot was starting material. An other spot, which had an R_f higher than that of the starting material, disappeared after working up the black reaction mixture.



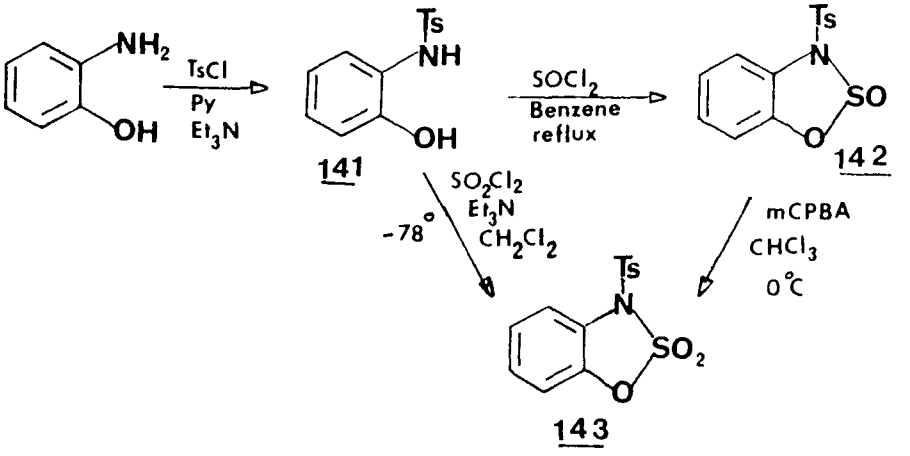
135

An attempt to prepare 136 was made using 2-(N-methyl)aminophenol which was synthsized as shown in the scheme 10.[111,112] Treatment of 140 with thionyl chloride lead to a black reaction mixture, no workup of this was attempted.



Scheme 16.
Synthesis of 2-(N-methyl)aminophenol.

By heating 2-(N-tosyl)aminophenol with thionyl chloride, Cupuano and coworkers[113] obtained 3-tosyl-1,2,3-benzoxathiazole-2-oxide 142 in 85 per cent yield. Cyclic sulfamate 143 was synthesized from 143 by oxidation (scheme 17).

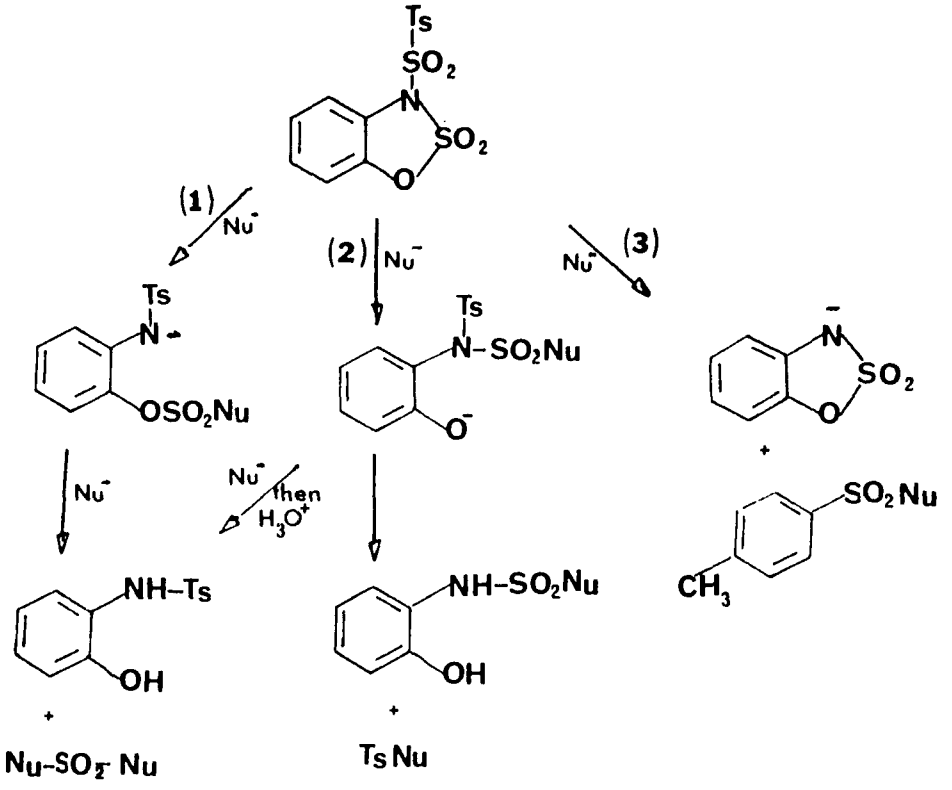


Scheme 17.
Synthesis of 3-tosyl-1,2,3-benzoxathiazole-2,2-dioxide.

After many trials with the oxidizing agents potassium permanganate, peroxytrifluoroacetic acid and m-chloro perbenzoic acid, the best oxidizing agent for converting 142 to 143 was found to be m-chloroperbenzoic acid in dry chloroform. The R_f of 142 and 143 are similar which makes their separation by chromatography difficult. Compound 143 could be separated from 142 using a mixture of hexane, ethyl acetate and THF (75:20:5% by volume). Silica gel column chromatography led to an isolated yield of 40-45%. Later 143 was synthesized by the reaction of 2-(N-tosyl)aminophenol (141) with sulfuryl chloride in the presence of trietnylamine[114] (scheme 17). If freshly

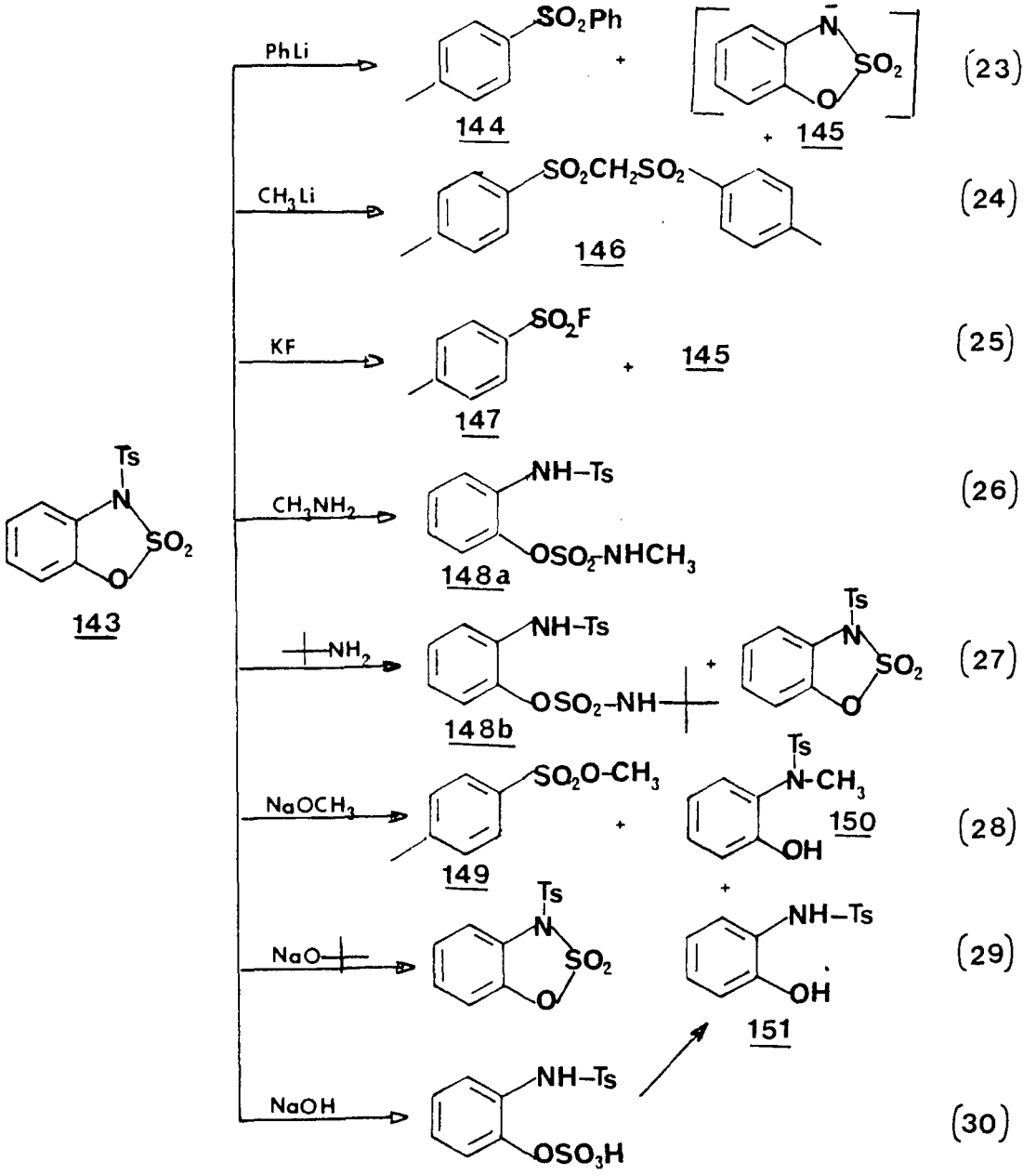
distilled sulfuryl chloride and dry triethylamine in dry dichloromethane was used, the reaction was clean and proceeded in good yield (70-75%).

There are at least three initial ways for cyclic sulfamate 143 to react with a nucleophile (scheme 18): (1) nucleophilic attack at ring sulfur with S-N bond cleavage, (2) nucleophilic attack at ring sulfur with S-O bond cleavage and (3) nucleophilic attack at sulfur of the tosyl group with displacement of the tosyl group.



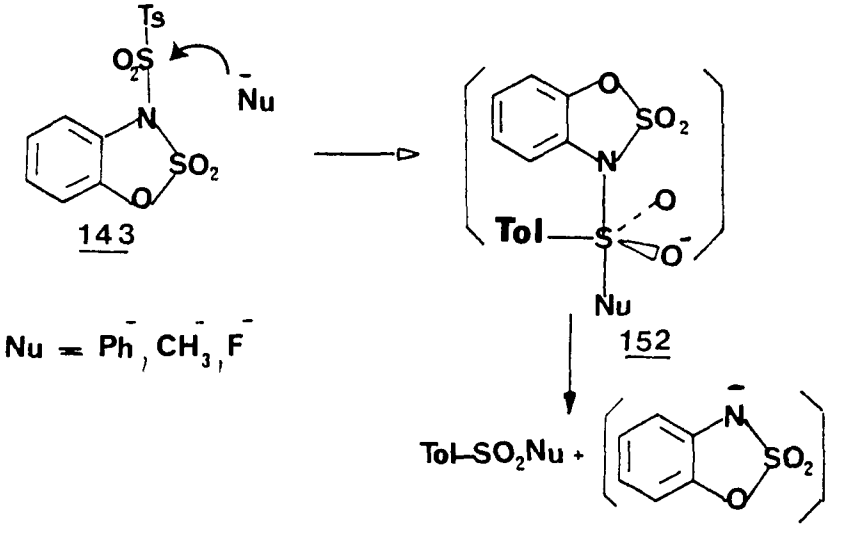
Scheme 18.
Some possible pathways for the reaction of 3-tosyl-1,2,3-benzoxathiazole-2,2-dioxide with nucleophiles.

The results of the reactions of cyclic sulfamate 143 with nucleophiles are shown in scheme 19.



Scheme 19.
The reaction of 3-tosyl-1,2,3-benzoxathiazole-2,2-dioxide with nucleophiles.

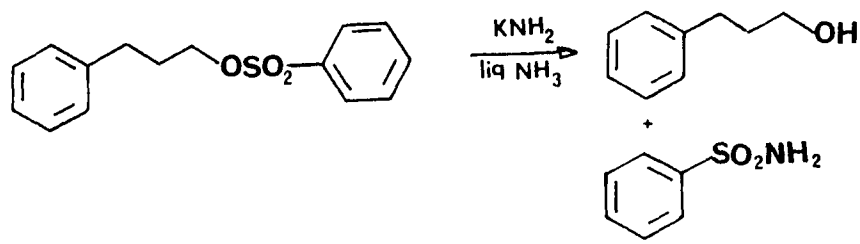
The isolation of phenyl p-tolyl sulfone (144), ditosylmethane (146), and 4-toluenesulfonyl fluoride (147) from the reaction of 143 with phenyllithium, methyllithium and potassium fluoride, respectively (eqs 23, 24 and 25), demonstrated that these reactions occurred via pathway 3 (scheme 18). The nucleophiles attacked at sulfur of the tosyl group and N-S bond cleavage occurred. Trigonal bipyramid 152 may be an intermediate in these reactions (scheme 20).



Scheme 20.
Reaction of phenyllithium, methyllithium and potassium fluoride with cyclic sulfamate 143 .

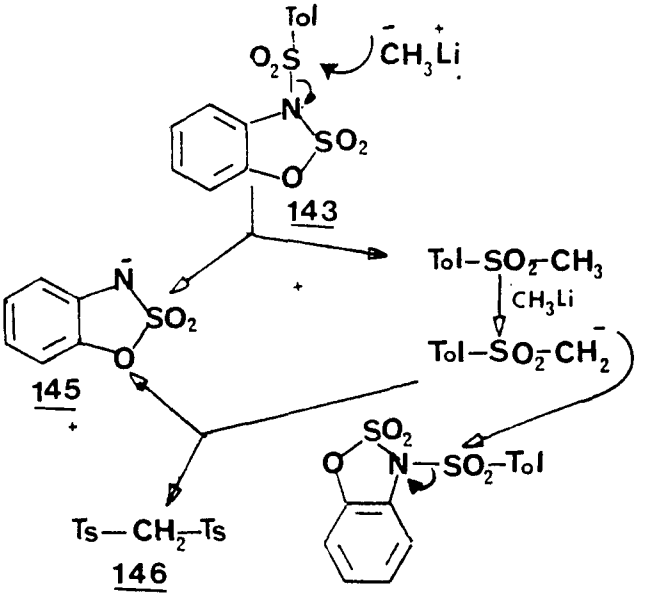
Nucleophilic substitution at sulfur of a tosyl group

is not an uncommon reaction. For example, it was reported[115] recently that reaction of 3-phenylpropyl benzenesulfonate with potassium amide in liquid ammonia gave 3-phenyl-1-propanol and benzenesulfonamide (eq 31).



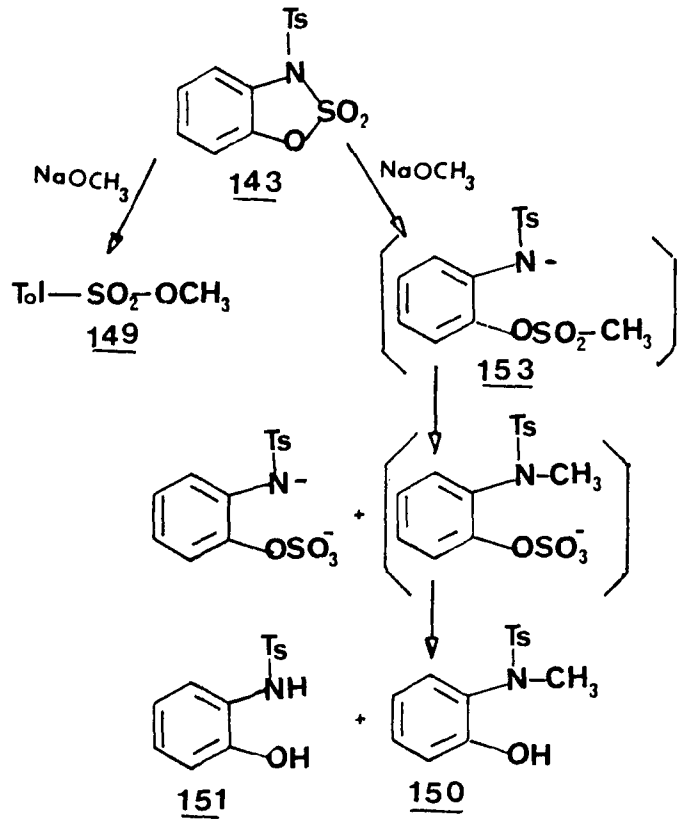
(31)

In the case of the reaction of 143 with methyllithium, the ditosylmethane may have been formed as shown in scheme 21. Compound 145 (see scheme 19) was also assumed to be formed, but attempts to trap it by adding methyl iodide, dimethyl sulfate, or methyl 4-toluenesulfonate were unsuccessful. It may have hydrolyzed to o-aminophenol or 2-N-methylaminophenol in the water layer which turned black upon standing. It is also conceivable that 145 could have lost SO_2 to yield the o-quinonimine anion.



Scheme 21.
Pathway for the reaction of 143 with methyllithium.

Reaction of 143 with sodium methoxide (eq 28, scheme 19) showed that both N-S bonds were cleaved. Methyl 4-toluenesulfonate (149) resulted from the attack of methoxide anion at sulfur of the tosyl group whereas 2-(N-tosyl) aminophenol (151) and 2-(N-methyl-N -tosyl)aminophenol (150) resulted from ring N-S bond cleavage (scheme 22). Presumbly 149 or 153 methylated nitrogen to eventually yield 150 . Starting material was recovered in quantitative yield when 143 was treated with sodium tert-butoxide (eq 29). Perhaps no or at least slow reaction occurred because of steric hindrance of the sodium-tert-butoxide or the low solubility of tert-butoxide in THF.

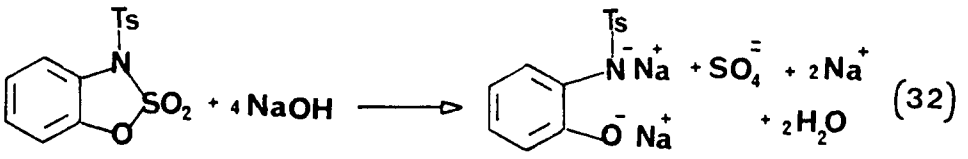


Scheme 22.
Reaction of 3-tosyl-1,2,3-benzoxathizole-2,2-dioxide with sodium methoxide.

The reaction of cyclic sulfamate 143 with methylamine and tert-butylamine in aqueous acetonitrile solution gave only ring S-N bond cleavage (eqs 26 and 27, scheme 19). Perhaps because of a steric effect, tert-butylamine reacted slowly with 143 and gave product 148b with recovery of starting material, whereas methylamine reacted more rapidly and gave only 148a and no recovered starting material. In

this case, any differences in steric effect between the nucleophiles did not cause any change in the position of bond cleavage.

When cyclic sulfamate 143 was reacted with aqueous sodium hydroxide, 2-(N-tosyl)aminophenol was obtained after acid workup. By adding barium chloride solution to the reaction mixture, an acid insoluble white precipitate of barium sulfate was formed which showed that sulfate anion was also produced in the hydrolysis. Pathways 1 and 2 in scheme 18 are possible routes for the alkaline hydrolysis of cyclic sulfamate 143 . N-tosylanilide and phenoxide are both good leaving groups, so it would be interesting to know if N-S or O-S bond cleavage or both occurred. If both S-O and S-N bonds were cleaved, four equivalents of sodium hydroxide would be needed to complete the reaction (eq 32).



(32)

A spectrophotometric titration was carried out to find the amount of base used in its reaction with cyclic sulfamate 143 (fig 8). Only two equivalents of sodium hydroxide were used, so only one bond was cleaved. Which bond was cleaved-

the S-O or the S-N bond- could not be determined by this tritation (eq 33).

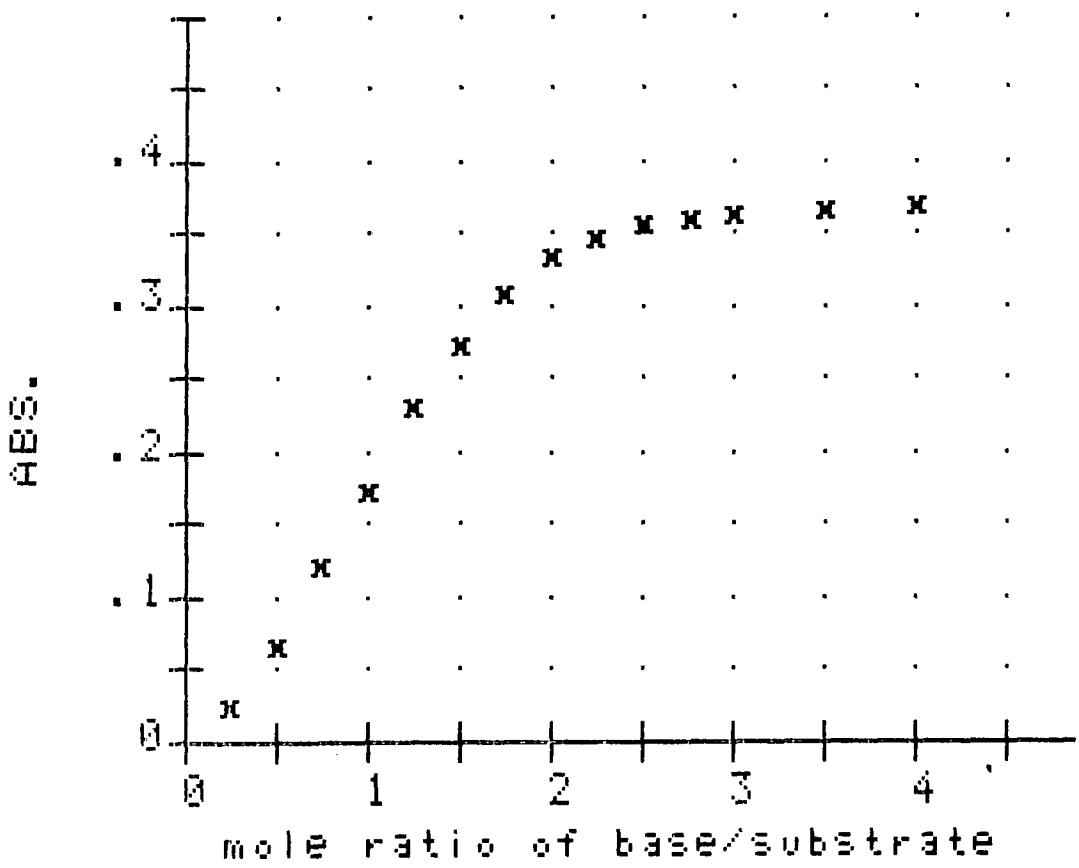
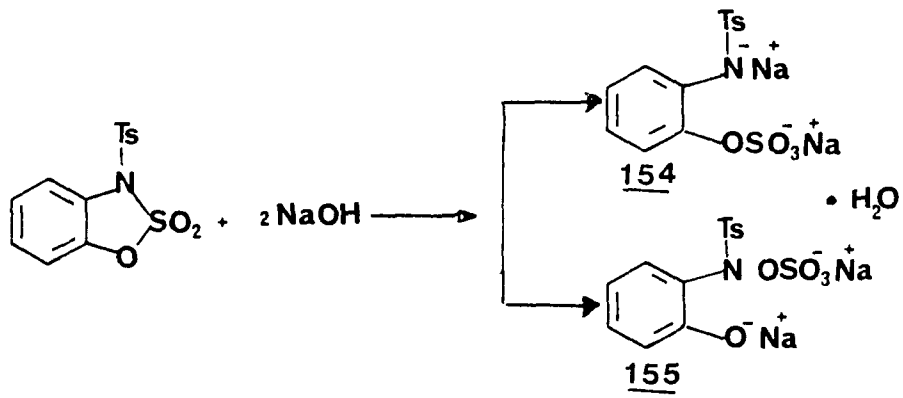


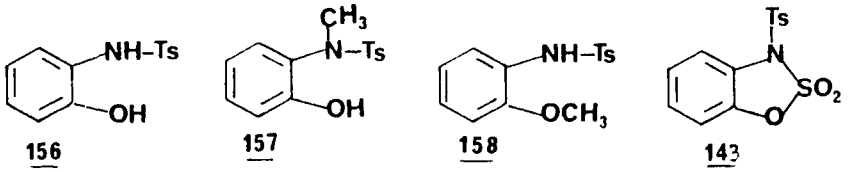
Figure 8.
Titration curve of 143 and NaOH.



(33)

The product sulfonate salt, 154 or 155 , was also isolated and its C,H and N analysis supported the correct empirical formula. Model compounds 156 , 157 and 158 were synthesized in order to compare their absorbances with the product, either 154 or 155 . The results are given in fig 9.

143, 156, 157, 158 + NaOH



156 157 158 143

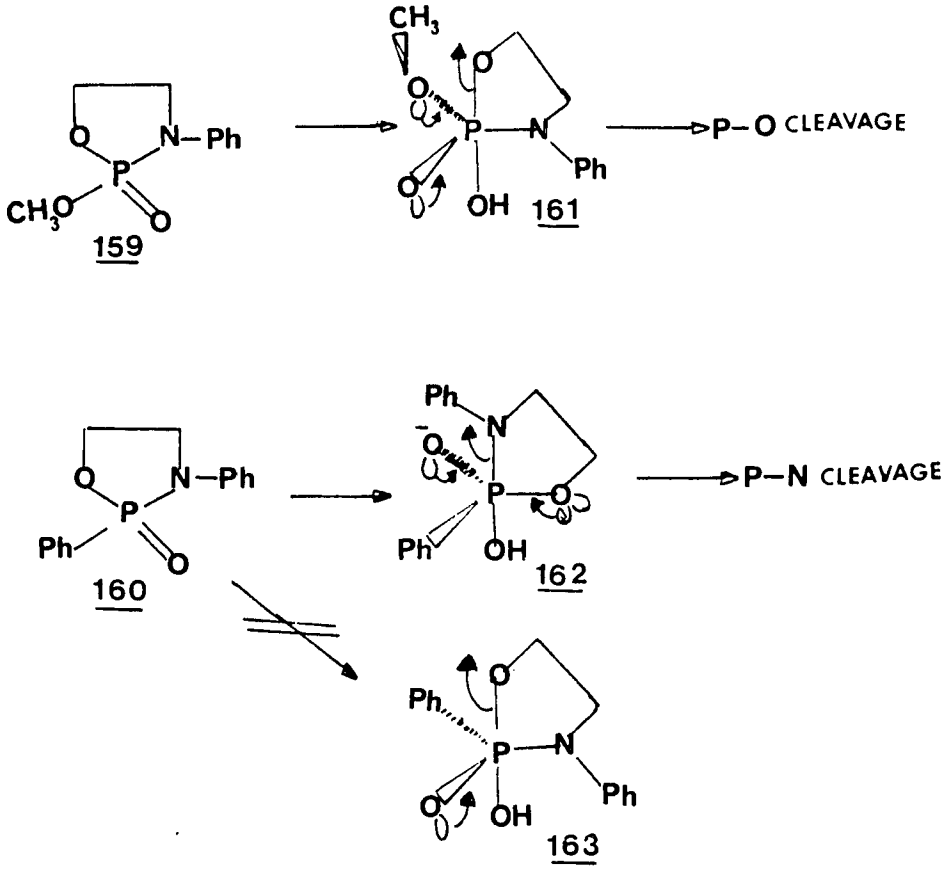
	156	157	158	143
λmax (nm)	299.0	301.0	284.0	284.2
	–	234.6	245.0	242.0
$\epsilon \times 10^{6}$	4.86	4.89	4.62	4.62

Figure 9.
λ max of compounds 143 and 156 - 158 + NaOH, solvent 83.3% H_2O, 0.05N NaOH, substrate concentration 6.15 x 10^{-5} mol.

All four compounds, 143 and 156 - 158 , at the same concentrations, were treated with 0.05N sodium hydroxide under the same conditions. The absorbance of hydrolyzed cyclic sulfamate 143 in sodium hydroxide solution is close to the absorbance of model compound 158 , so it is likely that the cleavage of the ring S-N bond occurred and 143 led to 154 as the product.

Gorenstein and coworkers[116] suggested that the dramatic difference between P-O bond and P-N bond cleavage

in cyclic phosphonamidates 159 and 160 could arise from stereoelectronic effects. These stereoelectronic effects involve the selective cleavage or formation of bonds which are trans or antiperiplanar (app) to lone electron pairs on directly bonded oxygen and nitrogen atoms (scheme 23).



Scheme 23.
Reaction of cyclic phosphonamidates with sodium hydroxide.

Phosphorane 161 , formed by hydroxide attack at tetrahedral phosphorus opposite to the ring oxygen of 159 , has two lone electron pairs on the oxygen antiperiplanar to the apical ester bond. This rearrangment facilitates ring P-O bond cleavage. Phosphorane 163 formed by hydroxide attack opposite to the ring oxygen of 160 has only one lone electron pair antiperiplanar to the apical ring oxygen. However, hydroxide attack opposite to the nitrogen atom yields phosphorane 162 in which the apical nitrogen is antiperiplanar to two oxygen lone pairs. Thus, P-N rather than P-O bond cleavage is stereoelectronically favored in the hydrolysis of 160 .[110,117] In phosphorane systems, the lone electron pair of a nitrogen, which is in the equatorial position, is favored to lie in the equatorial plane of the phosphorane[118] (Fig 10). The same may be true of oxygen, but it has two lone pairs, one of which will lie in the apical direction. Also, more electronegative ligands will assume the axial position in trigonal bipyramidal structures.[119]

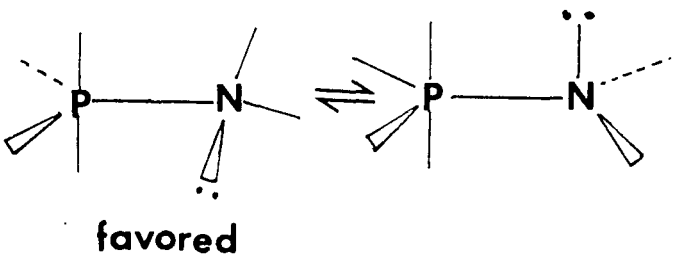
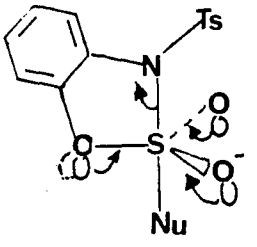
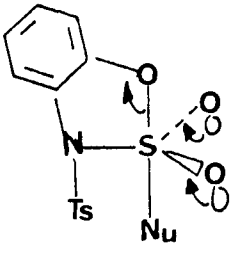


Figure 10.
Favored position of the lone pair of nitrogen in phosphorane.

Applying the above assumption in order to explain the reactivity of the cyclic sulfamate 143 , a trigonal bipyramidal structure analogous to the phosphoranes is first postulated as an intermediate or transition state.[3,10,18]



164

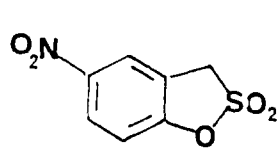


165

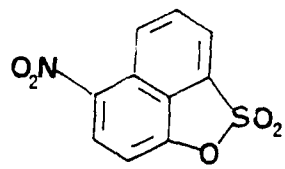
Sulfurane 164 was formed by nucleophilic attack opposite to the ring nitrogen. Three lone electron pairs in 164 are antiperiplanar to the ring S-N bond. In 165 two lone electron pairs on oxygen are antiperiplanar to the apical S-O bond whereas the lone pair of the equatorial nitrogen of 165 is conjugated with the benzene ring.[118] Thus, S-N bond cleavage will be favored stereoelectronically over S-O bond cleavage[28]. This may be a reason for ring S-N bond cleavage in the reaction of cyclic sulfamate 143 and the amines (eqs 26 and 27, scheme 19), and probably for the alkaline hydrolysis as well.

The nitrosulfonates 166 and 167 were proposed as

stable reagents for coupling in peptide synthesis.[120,121]

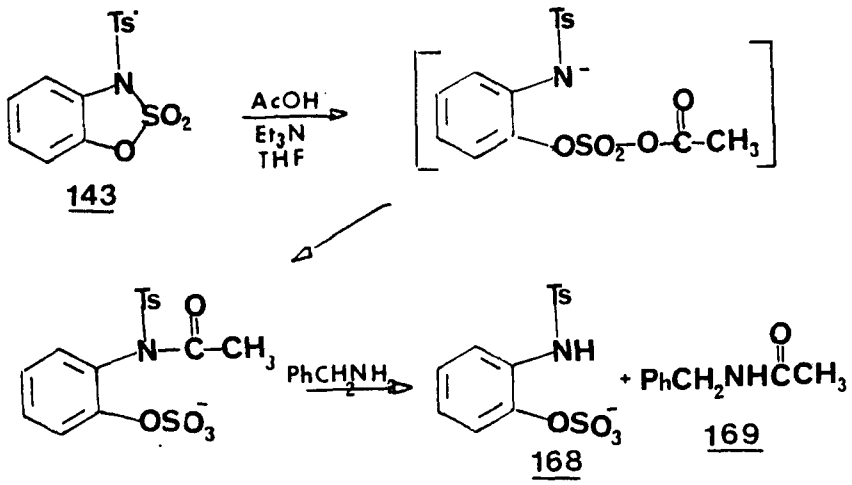


166



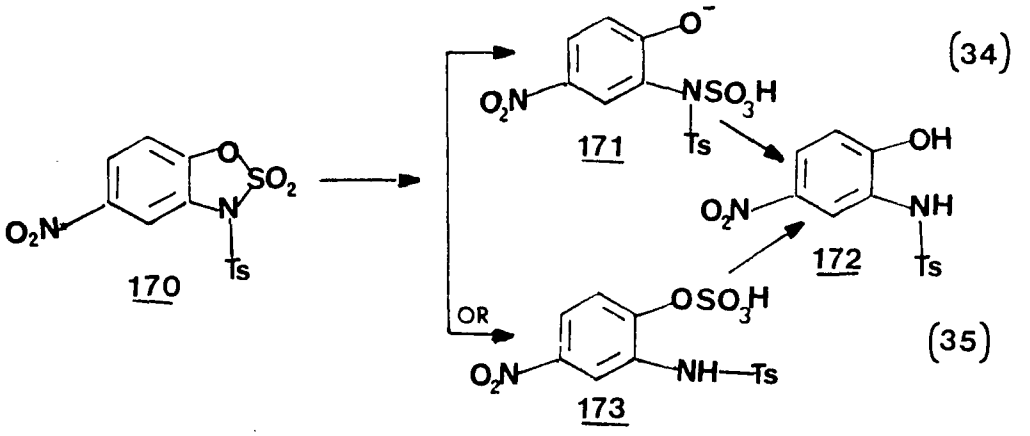
167

Cyclic sulfamate 143 was treated with a mixture of acetic acid and triethylamine at room temperature for 24 hours. TLC showed the absence of starting material. Next phenylamine was added. After seventy-six hours at room temperature the reaction was worked up and phenyl methyl acetamide 169 was recovered in 70-75 per cent yield (scheme 24). At a higher temperature (refluxing solvent) the reaction was complete in twenty-four hours. Under both conditions, attempted recovery of salt 168 from the water layer by acidification and extraction was unsuccessful. Perhaps addition of an amine such as diethylamine to the acidic water layer may permit recovery of the ammonium salt of 168 from the water layer by extraction.[121,122] Further study of the reaction is in progress.



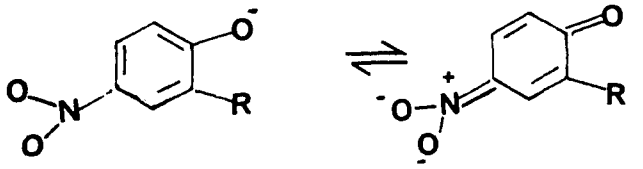
Scheme 24.
Amide synthesis using cyclic sulfamate 143 .

Compound 170 , which has a nitro group para to the ring oxygen was synthesized. Alkaline hydrolysis of 170 might give S-O bond cleavage 171 rather than S-N cleavage 173 (eqs 34 and 35). Compound 171 might be more stable than 173 because of resonance (eq 36).



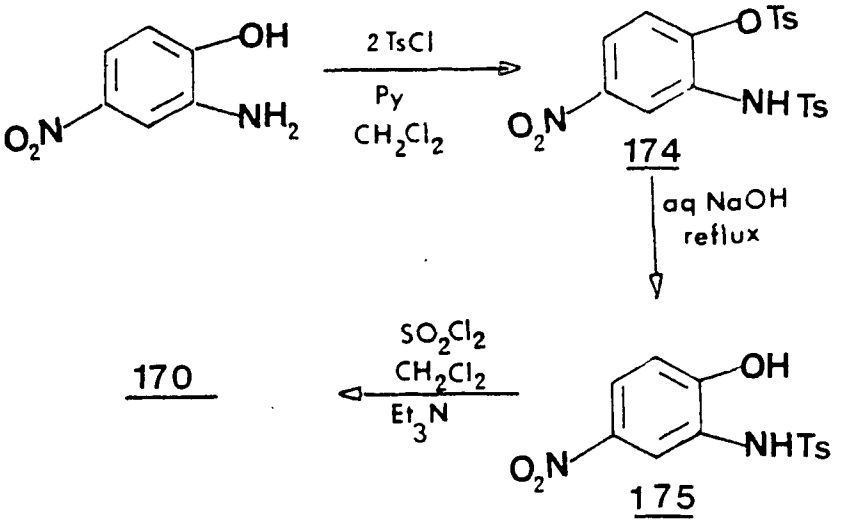
(34)

(35)



(36)

The synthesis of 170 was achieved by tosylation of 2-amino-4-nitrophenol at both nitrogen and oxygen. The tosyl group at oxygen was removed by hydrolysis in aqueous sodium hydroxide to give 2-(N-tosyl)-4-nitrophenol (175), which was cyclized with sulfuryl chloride in the presence of triethylamine to give a 75 per cent yield of 170 (scheme 25).



Scheme 25.
Synthesis of 3-tosyl-5-nitro-1,2,3-benzoxathiazole -2,2-dioxide.

The reaction of 170 with sodium hydroxide in a kinetic study produced a yellow solution with a λ max at 390 nm. Further study of this compound is under way.

A kinetic study has been done for both cyclic sulfamate 143 and 170 in order to compare the rates of their alkaline hydrolysis to the rates for acyclic and

cyclic sulfates and sulfonates.[52,54]

Kinetics Results and Discussion

Nucleophilic substitution at sulfur is generally second order kinetically.[60,75] The general expression for a second order reaction is shown in eq 37, where k_2 is the second order rate constant, [A] the concentration of substrate, and [B] the concentration of sodium hydroxide.

$$\text{Rate} = k_2[A][B] \qquad (37)$$

The intergrated rate expression for eq (37) is given by eq (38), in which Ao and Bo are the initial concentrations of substrate and sodium hydroxide, respectively, and x is the amount of A and B which have reacted.

$$1/(Ao-Bo)\ \ln\ Bo(Ao-x)/Ao(Bo-x) = kt \qquad (38)$$

If the sodium hydroxide concentration is held constant by keeping it in large excess during the reaction, the rate law will be pseudo first order (eq 39, where k_{obsd} is the observed pseudo first order rate constant).

$$\text{rate} = k_2[B](Ao-x) = k_{obsd} \qquad (39)$$

$$\text{rate} = k_{obsd}(Ao-x) \qquad (40)$$

$$k_2 = k_{obsd}/[B] \qquad (41)$$

Intergration of eq (39) gives:

$$\ln (Ao-x) = k_{obsd}\, t+c \qquad (42)$$

$$\text{or } \ln Ao/x = k_{obsd}\, (t-c) \qquad (43)$$

$$\text{or } \log x/Ao = -k_{obsd}/2.303\, (t-to) \qquad (44)$$

Concentration x appears in eq (44) as a logarithm, so a plot of log x vs t should be a straight line with a slope equal to $-k_{obsd}/2.303$.

Kinetic measurements of the alkaline hydrolysis of cyclic sulfamate 143 were performed in the uv-region using a Cary 219 spectrophotometer (fig. 11)

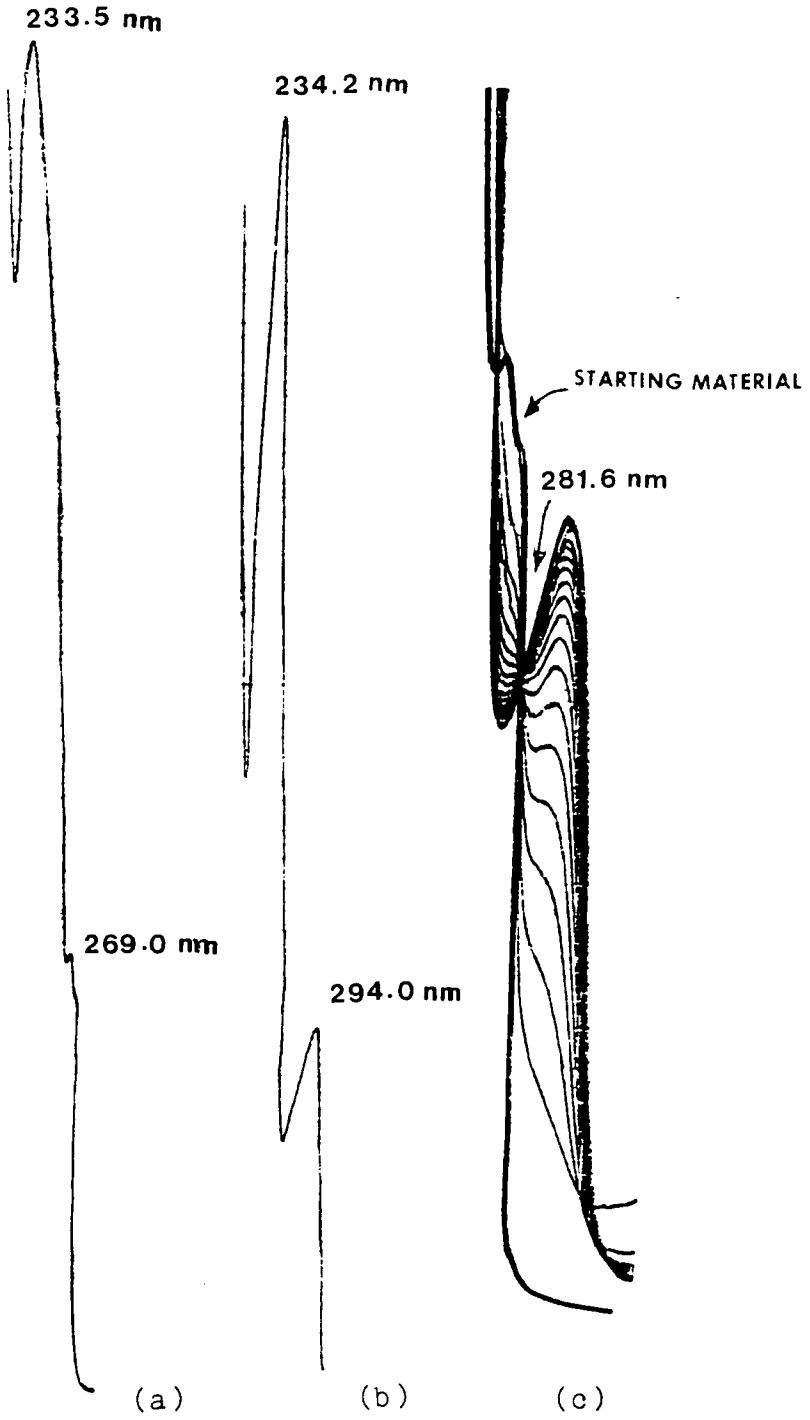


Figure 11.
(a) Absorbance of 143 . (b) Absorbance of the product of 143 + NaOH. (c) Repeated scans of 143 + NaOH at 14 C.

Repeated scans at 14° of cyclic sulfamate 143 plus sodium hydroxide in aqueous acetonitrile showed an isosbestic point, the wavelength at which the reactants and products have equal absorbance, at 281.6 nm. This indicates that no intermediate is present or that the intermediate does not exist long enough to build up enough concentration to be detected.[123]

Kinetic measurements were performed in aqueous acetonitrile (16.7% acetonitrile v/v). Acetonitrile was used to increase the solubility of the substrate in water. Appearance of the product peak at 294 nm was followed. The initial substrate concentration was 6.77×10^{-4} M and the concentrations of carbonate-free sodium hydroxide were 0.05, 0.06 and 0.10 N. All solvents were degassed by distillation under nitrogen. A Durrum-Gibson stopped flow spectrophotometer was used at 30 °C. The absorbance at infinity for every run was obtained at greater than ten half-lives. Table 3 gives the sample data obtained for a typical kinetic run.

Table 3.
A sample run of the alkaline hydrolyses of 3-tosyl-1,2,3-benzoxathiazole-2,2-dioxide at 20 °C.

Time(s)	Absorbance at time t(A_t)	$A_\infty - A_t$
1	0.125	0.148
2	0.145	0.130
3	0.155	0.118
5	0.180	0.093
7	0.195	0.078
9	0.210	0.063
12	0.228	0.045
15	0.240	0.033
19	0.250	0.023

Absorbance at infinity (A_∞) = 0.273
Concentration of NaOH = 0.05N
Concentration of substrate = 6.77×10^{-4} M

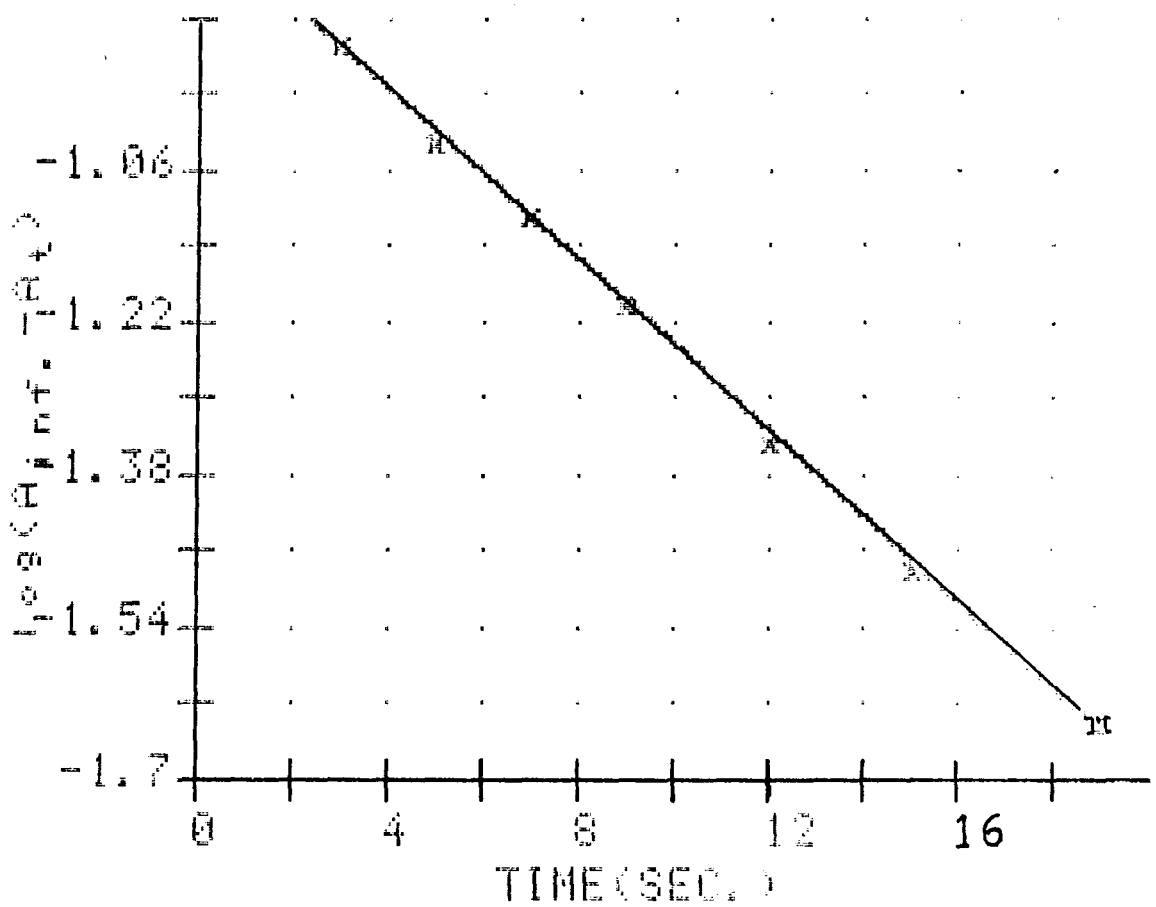
From eq (44)

$$\log (A_\infty - A_t) = -k_t/2.303 + \log (A_\infty - A_t) \quad (45)$$

Thus a plot of log ($A_\infty - A_t$) vs t gives

k_{obsd} = -2.303xslope.

A plot of log ($A_\infty - A_t$) vs t of the data in table 3 is shown in fig 12. A linear least-squares program run on an Apple IIe computer was used to generate the plot and calculate the parameters. Pseudo first order rate constants (k_{obsd}) obtained in this way are given in table 4.



Fitting Parameters

A = -.795101279

B = -.0451319047 = slope

Error of Estimate .017862786

Correlation Coefficient .968064893

Figure 12.
A plot of log (A_∞ - A_{obsd}) vs t for 143 from data of Table 3.

Table 4.

An average k_{obsd} and k_2 of alkaline hydrolyses of cyclic sulfamate 143 at difference temperature and base concentration.

Temperature (°C)	$[OH^-]$	k_{obsd} (s)	k_2 ($M^{-1}s^{-1}$)	t1/2
30	0.082	0.14	3.3±.02	5.1
	0.10	0.17	3.4±.13	4.1
	0.164	0.26	3.1±.14	2.9
20	0.050	0.090	1.7±.01	8.0
	0.060	0.11	1.8±.01	6.6
	0.10	0.18	1.8±.01	4.0
10	0.050	0.040	0.89±.01	16
	0.060	0.050	0.89±.01	13
	0.10	0.090	0.86±.02	8.0
0	0.050	0.020	0.35±0	40
	0.060	0.020	0.35±0	33
	0.10	0.040	0.36±.01	19

At 30 °C, the results are from stopped-flow apparatus. The average k_{obsd} was obtained from at least four runs.

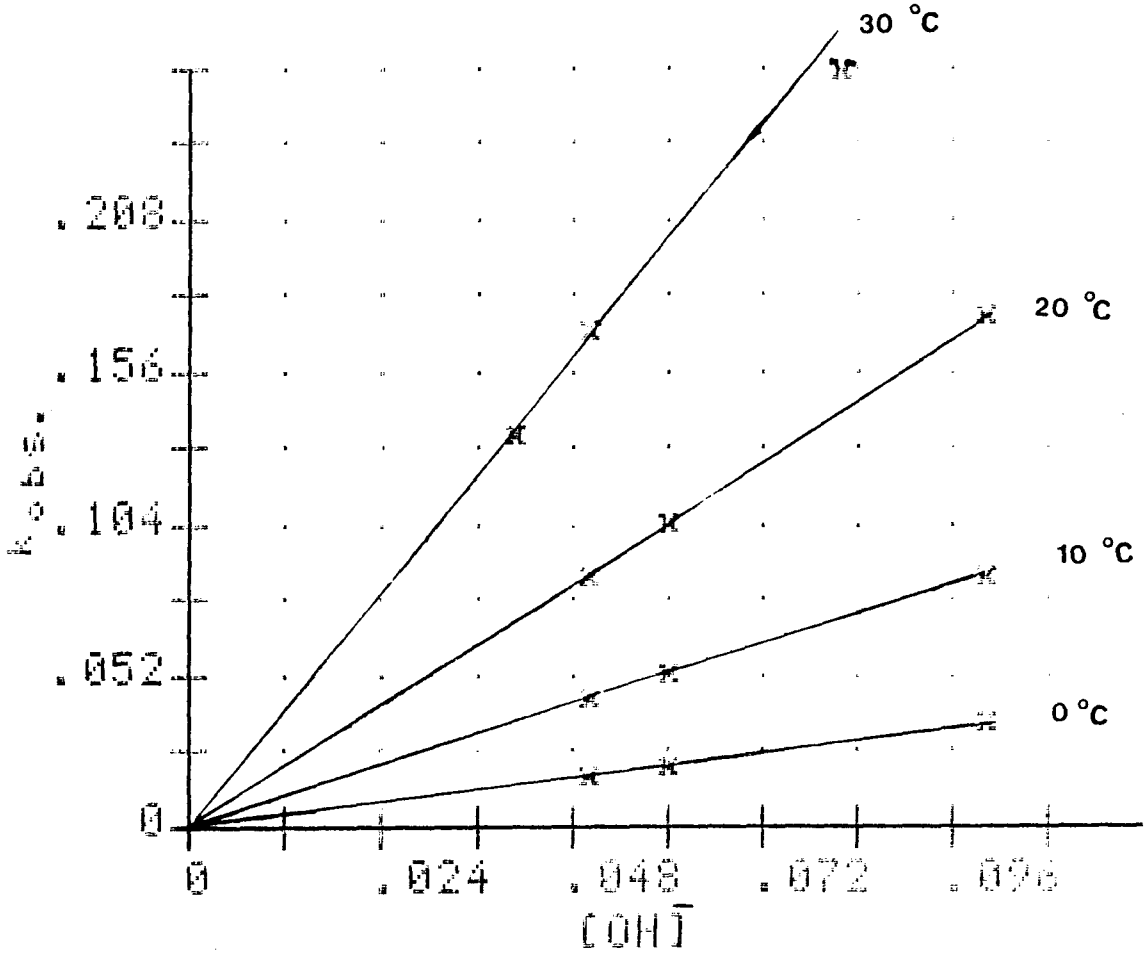


Figure 13.
A Plot of k_{obsd} vs $[OH]^-$

The results presented in table 4 and the straight line

of fig 13 which passes through the origin, indicate that the reaction is first order in cyclic sulfamate 143 and first order in hydroxide ion. The zero intercept in the plot of k_{obsd} vs $[OH]^-$ in fig 13 also indicates that the alkaline hydrolysis of 143 is an irreversible reaction and that there is no detectable hydrolysis by solvent alone.

At 25°C the rate of alkaline hydrolysis of cyclic sulfamate 143 is 2.2 $M^{-1}s^{-1}$ which is 8.5 times slower than for catechol cyclic sulfate 51 (18.8 $M^{-1}s^{-1}$) and 15 times slower than for 53 (36.6 $M^{-1}s^{-1}$) but about 4×10^7 times faster than for the acyclic sulfate 52 (fig 14). The rate constants for the alkaline hydrolysis of cyclic sulfamate 143 are in the same range as those for the alkaline hydrolysis of five-membered cyclic sulfates and sultones.

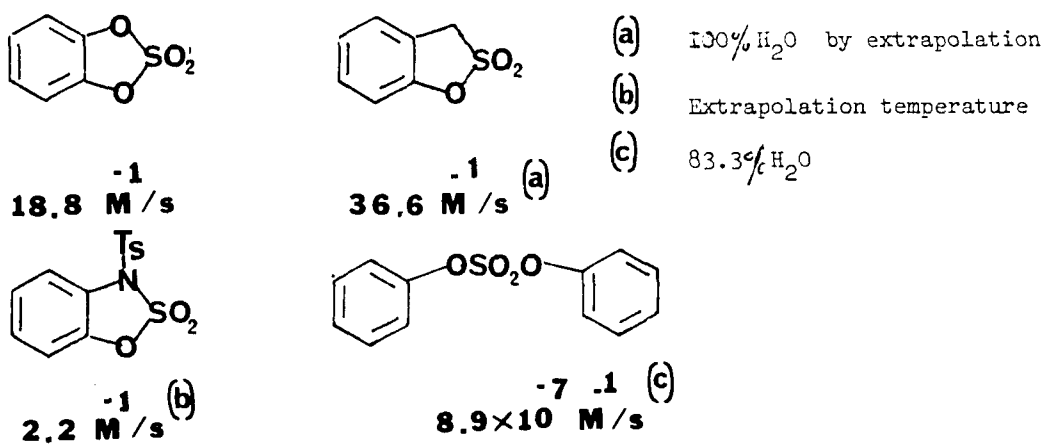


Figure 14.
Rate constants for the alkaline hydrolyses of a cyclic sulfate, a sultone, a cyclic sulfamate and an acyclic sulfate.

As mentioned before, acetonitrile was used as a co-solvent in the kinetic study. It was observed that increasing percentages of acetonitrile decreased the reaction rate (table 5). This observation is similar to the results of Kaiser who studied the rate of hydrolysis of cyclic sulfates and sultones,[59-61] no discussion of this observation was mentioned. Acetonitrile is a poor solvent for solvation.[124] By adding the polar solvent water the hydrolysis is easier, because of the effect of separation of the ion pairs.

Table 5.
Effect of solvent on the rate of alkaline hydrolyses of cyclic sulfamate 143 .

acetonitrile (% by volume)	75	50	25	16.7
rate ($M^{-1} s^{-1}$)	0.29	0.57	1.18	1.74

$[OH^-]$ = 0.05N

Temperature 20 °C

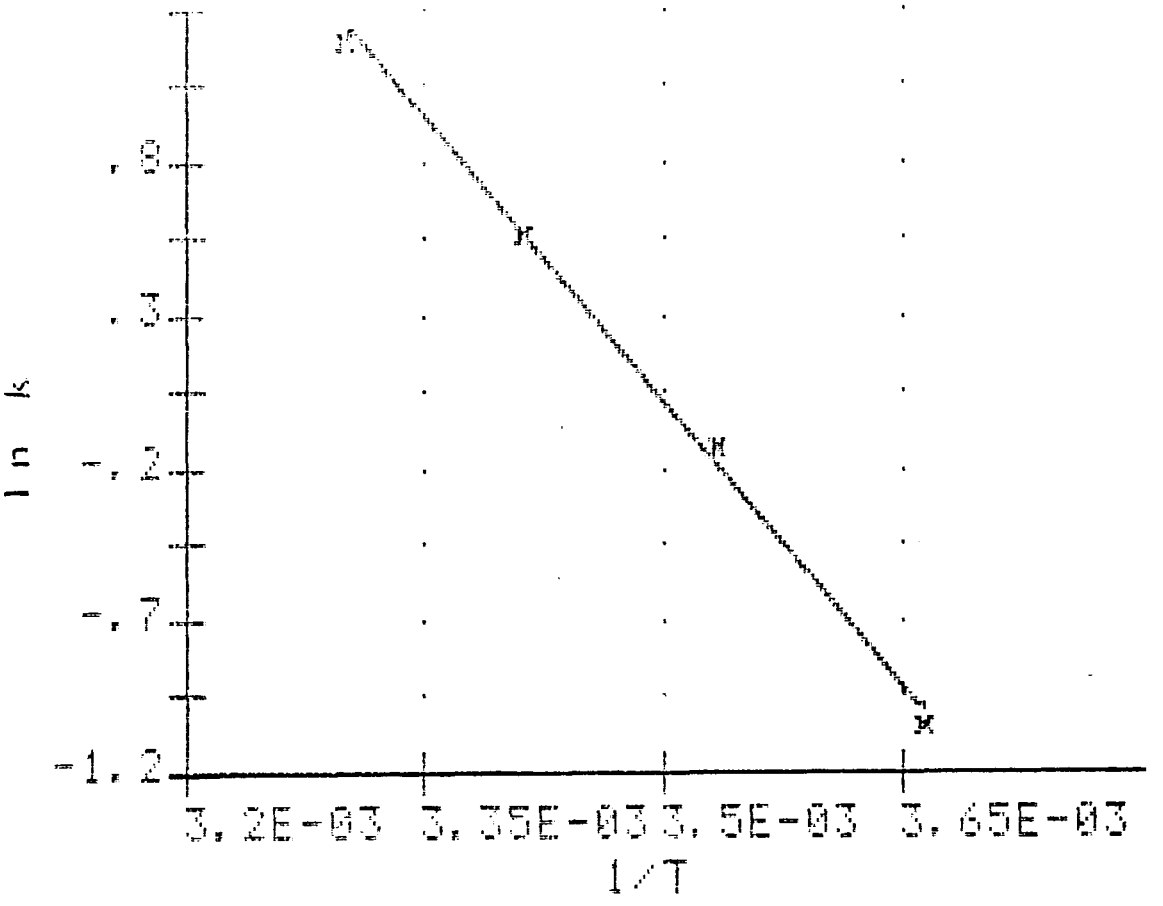
Tillet and coworkers[75] demonstrated that part of the difference in reactivity between the five-membered ring sultone 53 and a larger ring and acyclic analog arise from a combination of both enthalpy and entropy strain (see table 2, page 31). The enthalpy and entropy of activation

of cyclic sulfamate 143 were obtained from the rate data acquired at four temperatures. The variation of reaction rate with temperature is usually expressed by the Arrhenius equation which, in its integrated form, is given by eqs 46 and 47.

$$k = Ae^{-Ea/RT} \qquad (46)$$

$$\log k = \log A - Ea/2.303RT \qquad (47)$$

A plot of ln k vs 1/T has a slope of -Ea/R, where R is equal to 8.314 J/mol/K and Ea is the Arrhenius activation energy. The plot of ln k vs 1/T shown in Fig 15 has a slope of -6134.1 which leads to Ea = 51.00 kJ/mol.



Fitting Parameters
A = 21.4736654
B = -6134.12248 = slope

Error of Estimate .0726227851
Correlation Coefficient .938195508

Figure 15.
Plot of ln k vs 1/T for the alkaline hydrolyses of 143 .

The enthalpy of activation, $\Delta H^{\ddagger}$, can be calculated as

shown by eq 48. The entropy of activation, $\Delta S^{\ddagger}$, can be obtained from eq 49.

$$Ea = \Delta H^{\ddagger} + RT \qquad (48)$$

$$K = (kT/h)e^{\Delta S^{\ddagger}/R} \cdot e^{\Delta H^{\ddagger}/RT} \qquad (49)$$

Taking logarithms and rearranging eq 49 gives eq 50. where k is the Boltzmann constant, 1.38×10^{-3} J/K and h is Planck's constant, 6.63×10^{-3} J/s. The entropy and enthalpy of activation given in table 6 are calculated from eqs 48 and 49.

$$\Delta S^{\ddagger}/2.303R = \log K - \log(ek/h) - \log T + Ea/2.303Rt \qquad (50)$$

Table 6.
$\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ value at different temperatures.

Temperature($^{\circ}$C)	H (kJ/mol)	S (eu)
30	53.52±.13	-75.19±.83
20	53.43±.04	-73.99±.37
10	53.35±.04	-73.88±.48
0	53.27±.12	-74.38±.02

The values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for the hydrolysis of 143 are close to those of the five-membered ring sultone 55 (table 2, page 31).[75] That is, the alkaline hydrolysis of cyclic sulfamate 143 may follow the same mechanism as the

hydrolysis of sultone 53 . The negative entropy of activation indicates that the transition state is more ordered than the ground states of the separate reactants.

The kinetic study of 170 was carried out by using a Durrum-Gibson stopped flow spectrophotometer and following the appearance of the the product peak at 440 nm. The results at 30° are given in table 7. Further kinetic study of this compound is in progress.

Table 7.
k_{obsd} and k_2 of 170 + NaOH.

Run no	$[OH^-]$	k_{obsd}	k_2 (M^{-1} s^{-1})
1	0.0252	0.0650	50.9+2.13
2		0.659	
3		0.663	
4		0.662	
5		0.610	
6		0.599	
average		0.641	
1	0.0505	1.31	52.4+.62
2		1.32	
3		1.33	
4		1.32	
average		1.32	
1	0.0757	1.94	51.4+1.62
2		2.04	
3		1.91	
4		1.97	
average		1.97	
1	0.0152	0.422	57.4+4.34
2		0.434	
3		0.455	
4		0.433	
average		0.436	

concentration of substrate = 1.50×10^{-4}M
Solvent 50% acetonitrile-water v/v

In conclusion, the rate of alkaline hydrolysis of sulfamate 143 is approximately the same as those reported for the hydrolyses of structurally similar sulfate 51 and sultone 53 . In addition, the enthalpies and entropies of activation observed for 51 and 143 are similar which suggests that their mechanisms for hydrolysis are also similar. Ring S-N bond cleavage occurred when sulfamate 143 was treated with hydroxide ion, methylamine, or t-butylamine, whereas the S-N bond exo to the ring was cleaved when 143 was treated with phenyllithium, methyllithium, or potassium fluoride. Treatment with potassium t-butoxide resulted in cleavage at both S-N bonds. In view of the greatly increased reactivity towards hydroxide ion of the cyclic esters 51 and 53 over that of their acyclic analogs, the cases of exo S-N bond cleavage, rather than ring cleavage, were unexpected and are, as yet, unexplained. Replacement of the tosyl group in 143 by some non-displaceable group, such as a phenyl radical, should be carried out to see which ring bond, S-N or S-O, is cleaved now by the various nucleophiles and, for hydroxide ion, at what rate it occurs.

Since sulfamate 143 is easy to prepare from cheap starting materials and is capable of acting as a coupling reagent in amide synthesis from an acid and an amine, its use for this purpose, and perhaps also in ester synthesis, should be explored.

EXPERIMENTAL

Instrumentation NMR spectra were recorded on Varian 360 A (^{1}H) and JEOL FX90Q (^{1}H and ^{13}C) spectrometers. Spectra were referenced to internal TMS. Infrared spectra were recorded on a Perkin Elmer 283B spectrophotometer. Ultraviolet spectra were recorded on a Varian-Cary 219 double beam programable spectrophotometer equipped with a temperature controlled bath and on a Durrum-Gibson stopped flow spectrophotometer with a .02 m path-length cuvette and a Kel-F flow-path. Mass spectra were obtained on a Hitachi-Perkin-Elmer RMU-6E mass spectrometer by University of New Hampshire Instrumentation center personnel. Elemental analysis were performed at the University of New Hampshire Instrumentation center using a Perkin Elmer 240B Elemental analyser.

Materials All chemicals were reagent grade. THF and diethyl ether were treated with calcium hydride and then distilled under nitrogen from sodium benzophenone ketyl. Methylene chloride and hexane were distilled under nitrogen from calcium hydride. Chloroform was distilled from phosphorus pentaoxide. Pyridine and triethylamine were distilled from potassium hydroxide. Thin layer chromatography (TLC) was performed on aluminum TLC sheets, precoated with silica gel 60F-254, made by E. Merck. Preparative layer chromatography plates were made with

silica gel 60PF-254 (E. Merck) on glass plates and were activated at 100°C for two hours. Glassware was dried by heating in an oven for at least twenty-four hours and was cooled under nitrogen.

1,1-Dioxy-3-chloro-3H-2,1-benzoxathiole [1] was prepared in quantitative yield according to the procedure given in Yildiz's dissertation:[1] mp 113 °C; IR spectrum no. 3909 (Nujol) 1150 and 1445 cm^{-1} (s, SO_2); ^1H NMR spectrum no 6772 ($CDCl_3$) δ 8.00-7.50 (m, 4H, ArH), 7.28 (s, 1H, CHCl).

o-Tolyl Sultone [1] was prepared in 65.48 per cent yield according to the procedure given in Yildiz's dissertation:[1] mp 112-113 °C; IR spectrum no. 3907 (Nujol) 1150 and 1450 cm^{-1} (s, SO_2); ^1H NMR spectrum no 6794 ($CDCl_3$) δ 8.00-7.30 (m, 4H, ArH), 5.60 (s, 2H, CH_2).

Sodium 4-toluenesulfinate Dihydrate [1] was prepared in 93 per cent yield by the procedure given in Yildiz's dissertation:[1] mp was greater than 300 °C; IR spectrum no 9399 (KBr) 3420 (br, H_2O), 1020 cm^{-1} (s, SO); ^1H NMR spectrum no 8805 (D_2O) δ 7.71-7.22 (AA'BB', 4H, ArH), 2.41 (s, 3H, CH_3).

Sodium 2-(4'-toluenesulfonyl)methylbenzenesulfonate[1] was synthesized in 80 per cent yield by the procedure given in Yildiz's dissertation:[1] IR spectrum no 3908 (KBr) 1300 and 1100 (s, SO_2), 1250, 1220, 1140 cm^{-1} (s, SO_3); ^1H NMR spectrum no 8864 (D_2O) δ

8.19-7.20 (m, 8H, ArH), 5.15 (s, 2H, CH_2),2.42 (s, 3H, CH_3).

2-(4'-Toluenesulfonyl)methylbenzenesulfonyl Chloride[1] was prepared in 85.1 per cent yield by the procedure given in Yildiz's dissertation:[1] mp 135-136 °C; IR spectrum no 3906 (KBr) 1145, 1165, 1290, 1310, 1370 cm^{-1} (s, SO_2Cl and SO_2). ^1H NMR spectrum no δ 8863 ($CDCl_3$) δ 8.30-7.20 (m, 8H, ArH), 4.99 (s, 2H, CH_2), 2.42 (s, 3H, CH_3).

Bis-2-(4'-Toluenesulfonyl)methylphenyl Disulfide (89). [125] Sodium iodide (7.5g, 50 mmol) was suspended in a solution of chlorotrimethylsilane (2.75g, 25.0 mmol) in methylene chloride (25 mL) containing a catalytic amount of tetra-n-butylammonium iodide (100mg). 2-(p-Toluenesulfonyl)methylbenzene sulfonyl chloride (1.79g, 5.00 mmol) was added and the mixture was stirred for sixteen hours at room temperature. The mixture was poured into a solution of sodium bicarbonate and iodine was removed by the addition of a saturated solution of sodium thiosulfate. The mixture was extracted twice with 25mL portions of methylene chloride. The extracts were dried over anhydrous magnesium sulfate and the solvent was removed to yield a crude yellow product. Purification by silica gel column chromatography afforded 0.670 g (77.9%): mp 189-190 °C (reported[1] mp 190-191 °C); IR spectrum no 5397 (KBr) 1320 and 1145 cm^{-1} (s, SO_2). ^1H NMR spectrum no 7490 ($CDCl_3$) δ 7.69-7.12 (m,

8H, ArH) 4.38 (s, 2H, CH_2), 2.41 (s, 3H, CH_3).

Reaction of Bis-2-(4'-Toluenesulfonyl)methylphenyl Disulfide with Sodium Hydride. Sodium hydride, 50% dispersion in mineral oil, (0.361g, 9.00 mmol) was placed in a flame-dried 100 mL three-necked round-bottomed flask equipped with a magnetic stirrer. The flask was then capped with a rubber septum and flushed with nitrogen. The sodium hydride was washed five times with dry hexane by using a syringe. After adding dry THF (10 mL) to the flask, the flask was placed in a Dry Ice-acetone bath. The solution of 2-(4-toluenesulfonyl)methylphenyl disulfide (1.0g, 1.8 mmol) in dry THF (60 mL) was added at -78 ^{o}C by syringe. The progress of the reaction was followed by TLC. After one hour the reaction mixture was allowed to warm to room temperature. The reaction mixture was cloudy after fifteen min at room temperature. After twenty hours, the TLC was the same as at five hours. (ca. 50% remaining starting material). Water (0.25 mL) was added to the reaction mixture until gas evolution ceased. The white precipitate was filtered, the THF was removed under reduced pressure, and the residue was extracted four times with methylene chloride (20 mL). The methylene chloride layer was dried over anhydrous magnesium sulfate, filtered, and concentrated under reduced pressure to give 0.0640g of white solid. The white precipitate (.1619g) gave: mp greater than 300 ^{o}C; IR spectrum no 2610 (KBr) 1050 cm^{-1} (s, SO); ^{1}H NMR Spectrum No 7647 (D_2O) δ

7.15-1.28 (AA'BB', 4H, ArH), 2.38. (S, 3H, CH_3). This product was identified as sodium 4-toluenesulfinate by comparison with mp and spectra from published data (Sadtler spectrum 4457 (NMR), 13486 (IR)). The white solid from the methylene chloride layer gave: mp 213-214 °C (lit[131] mp 215 °C); positive test for sulfur with sodium fusion; IR spectrum no 2608 (KBr) 1452, 1350 (m), 736 and 710 cm^{-1} (s); ^1H NMR spectrum no 7041 ($CDCl_3$) δ 8.1-7.79, 7.63-7.25 (m); ^{13}C NMR spectrum no 4818 ($CDCl_3$) δ 142.3, 133.4, 133.1, 124.9, 124.0, and 121.6; MS no 582 m/e (rel intensity) 240 (1000, M^+), 241 (167, M+1), 242 (99, M+2), (calcd 241 (168, M+1), 242 (99, M+2)); Anal. Calcd for $C_{14}H_8S_2$: C, 70.00; H, 3.33. Found: C, 67.85; H, 3.33. This compound was identified as [1] benzothieno [3,2-b][1] benzothiophene (91) from the above data.

1-Butanesulfenyl Chloride.[126] 1-Butanethiol (9.02g, 0.100 mol) was dissolved in heptane (25 mL) in a 250 mL round-bottomed flask provided with a magnetic stirrer. The flask was placed in an ice bath. Chlorine (7.25g, 0.100 mol), which had been condensed in a tared flask placed in a Dry Ice-acetone bath, was bubbled into the solution via a glass tube placed below the surface. The resulting solution of sulfenyl chloride was used directly to prepare N-(butanethio)phthalimide.

N-(n-Butanethio)phthalimide (92).[95] Phthalimide (14.7g, 0.100 mol), triethylamine (15g, 0.15mol) and

dimethylformamide (60 mL) were placed in a 250 mL round-bottomed flame-dried flask equipped with a magnetic stirrer and an addition funnel. The flask was placed in an ice bath and the system was flushed with nitrogen. Under an atmosphere of nitrogen, the solution of 1-butane sulfenyl chloride, made above, was placed in the addition funnel and added dropwise to the stirred phthalimide solution. The reaction mixture was stirred for thirty min at 0 °C and then transferred to a 1-L beaker to which ice water (750 mL) was added. The product precipitated and was collected by suction filtration to give a yellow solid. Recrystallization from 95% ethanol gave 9.30g (54.7%): mp 63 °C (lit[95] 65 °C; IR spectrum no 2392 (KBr) 1750, 1710 , 1280, 1050, 700 cm^{-1}; ^1H NMR spectrum no 6775 ($CDCl_3$) δ 7.9(m, 4H, ArH), 2.92 (t, 2H, CH_2), 1.90-0.70 (m, 9H, n-Bu).

Attempted Synthesis of 2-Aminophenyl Butyl Disulfide (93). [126] N-(n-butylthio)phthalimide (2.35g, 0.0100 mol) was dissolved in benzene (40 mL) in a 100 mL round-bottomed flask equipped with a magnetic stirrer. o-Aminothiophenol (1.25g, 0.0100 mol) was added to this mixture. A white precipitate formed immediately. After the reaction was complete (twenty min, TLC), the precipitate was filtered. The filtrate was concentrated under reduced pressure. Purification by silica gel column chomatography gave 0.25g (20%) of yellow solid: mp 89-90 °C; IR spectrum no 5463 (KBr) 3380, 3300, 1610, 1470, 1445, 1300,

745 cm^{-1}; ^{1}H NMR spectrum no 6789 ($CDCl_3$) δ 7.46-6.45 (m, 8H, ArH), 4.33 (br, 4H, NH_2); ^{13}C NMR spectrum no 6503 ($CDCl_3$) δ 148.5, 130.7, 131.5, 118.7, 118.2, 115.1; MS no 475 m/e 248 (142, M^+), 249 (34, M+1). The compound was identified as bis-2-aminophenyl disulfide (94) from the above spectra.

Reaction of Bis-2-Aminophenyl Disulfide with Sodium Hydride. Sodium hydride (0.192g, 5.00 mmol) was placed in an oven-dried three-necked round-bottomed flask equipped with a magnetic stirrer. The flask was capped with rubber septums and the system was flushed with nitrogen. By using a syringe, the sodium hydride was washed five times with dry hexane. Dry ether (5 mL) was added to the flask. Then a solution of 2-aminophenol disulfide (.15g, 0.60 mmol) in ether (5 mL) was added by syringe. After twenty four hours, TLC showed only starting material. The temperature was increased to 30 °C, but no change in the TLC was apparent. The reaction mixture was quenched with water, the precipitate filtered and the filtrate extracted with dichoromethane. The extract was dried over anhydrous magnesium sulfate. Evaporation of the dichloromethane under reduced pressure gave a solid which was identified as starting material by TLC.

2-Methylthioaniline (98). [97] 2-Mercaptoaniline (30g, 0.24 mol) was dissolved in absolute ethanol (125 mL) in a 250 mL round-bottomed flask equipped with a magnetic stirrer. Sodium (5.4g, 0.24mol) was added in small pieces

followed by methyl iodide (35g, 0.24 mol). The reaction mixture was refluxed for forty min, then cooled and poured into water (1 L). The mixture was extracted twice with 25 mL portions of ether. The ether extracts were dried over anhydrous sodium sulfate. Concentration under reduced pressure gave an oily yellow product which was purified by distillation at 75 °C (0.05 mm) to give 23.05g (69.56%): IR spectrum no 2467 (neat) 3470 and 3350 cm^{-1} (S, NH_2); ^1H NMR spectrum no 8117 ($CDCl_3$) δ 7.50-6.50 (m, 4H, ArH), 4.22 (br, 2H, NH_2), 2.28 (s, 3H, CH_3)

2-(Methylthio)acetanilide (99).[127]

2-Methylthioaniline (30.3g, 0.200 mol) in glacial acetic acid (30.0 mL) and water (21.7 mL), was placed in a 250 mL three-necked round-bottomed flask equipped with a magnetic stirrer and a thermometer. After being stirred for five min, ice (35g) was added. When the temperature reached 0-5 °C, acetic anhydride (10.3 mL, 0.210 mol) was added all at once with rapid stirring. The temperature rose to 15 °C after which the flask was heated on a steam bath. After six hours, TLC showed the presence of considerable starting material so one more equivalent of acetic anhydride was added together with triethylamine (2 mL). After one more hour on the steam bath, the reaction mixture was allowed to cool over night. A white solid was obtained and recrystallized from 50% ethanol-water to give 27.4g (70%): mp 103-104 °C; IR spectrum no 5400 (KBr) 3200

(s, NH), 1625 cm^{-1} (s, CO); ^1H NMR spectrum no 7652 ($CDCl_3$) δ 8.50-8.00 (br, 1H, NH), 7.50-6.90 (m, 4H, ArH) 2.28 (s, 3H, CH_3), 2.38 (s, 3H, CH_3).

2-(Methylsulfonyl)acetanilide (100).[98] 2-(Methylthio) acetanilide (5.0g, .028 mol), acetic acid (100 mL) and 30% hydrogen peroxide (12 mL, 0.14 mol) were placed in a 100 mL round-bottomed flask equipped with a magnetic stirrer. The reaction mixture was stirred for four days after which it was poured into water (50 mL). The mixture was extracted with dichloromethane, and the extract was dried over anhydrous magnesium sulfate. The solvent was removed under reduced pressure to give a solid which was recrystallized from ethanol to yield 5.61g (61.0%): mp 245-246 °C; IR spectrum no 5401 (KBr) 3320 (s, NH), 1675 (s, CO), 1305 and 1125 cm^{-1} (s, SO_2); ^1H NMR spectrum no 7661 ($CDCl_3$) δ 9.61 (br, 1H, NH), 8.68-7.10 (m, 4H, ArH), 3.31 (s, 3H, CH_3), 2.25 (s, 3H, CH_3).

2-(Aminophenyl) Methyl Sulfone (101).[98] A mixture of 2-(methylsulfonyl)acetanilide (16.03g, .07600 mol) and 40% aqueous sodium hydroxide (20 mL) was heated to 60 °C for thirty min and then was allowed to cool to room temperature. The mixture was extracted twice with dichloromethane and the extracts were dried over anhydrous magnesium sulfate. After removal of the dichloromethane, a white solid was obtained, 12.90g (quantitative yield). Recrystallization from ethanol gave: mp 84-85 °C; IR

spectrum no 5265 (KBr) 3495 and 3390 (s, NH_2), 1290 and 1130 cm^{-1} (s, SO_2); ^1H NMR spectrum no 8157 ($CDCl_3$) δ 7.91-6.68 (m, 4H, ArH), 5.12 (br, 2H, NH_2), 2.05 (s, 3H, CH_3); ^{13}C NMR spectrum no 5698 ($CDCl_3$) δ 146.3, 135.1, 129.1, 128.0 121.6, 118.8, 117.7 and 42.1.

2-Bromophenyl Methyl Sulfone (103).

2-(Aminophenyl)methyl sulfone was diazotized and then reacted with cuprous bromide according to the procedure in the literature.[100] Recrystallization from 95% ethanol gave yellow solid in 50 per cent yield: mp 106-107 °C; IR spectrum no 5261 (KBr) 1310 and 1150 cm^{-1} (s, SO_2); ^1H NMR spectrum no 8225 ($CDCl_3$) δ 8.38-8.13 and 7.93-7.50 (m, 4H, ArH), 3.30 (s, 3H, CH_3); ^{13}C NMR spectrum no 5727 ($CDCl_3$) δ 139.6, 135.3, 134.7 131.0, 126.1 and 120.5; MS no 438, m/e (rel. intensity) 235 (196, M^+), 237 (160, M+2).

Attempted Synthesis of 2-(Mercaptophenyl) Methyl Sulfone (102). 2-(Aminophenyl)methyl sulfone was diazotized and then reacted with potassium ethyl xanthate according to the procedure in the literature[102]. More than seven spots were observed by TLC. No attempt was made to isolate the product.

Attempted Synthesis of Bis-2-methylsulfonylphenyl Disulfide (104). [101] A solution of 2-bromophenyl methyl sulfone (0.300g, 1.28 mmol) in warm ethanol was added to a mixture of sulfur (0.320g, .0100mol) and sodium sulfide

(1.5g, .017 mol) in water (25 mL). The mixture was heated at reflux for thirteen hours. The ethanol was removed under reduced pressure and then the mixture was filtered to remove unreacted material. The filtrate was poured into conc. hydrochloric acid (5 mL) and ice whereupon a precipitate was formed. Extraction of this material with boiling chloroform gave a solid which was identified as starting material by TLC. ^{1}H NMR spectrum no 8282 ($CDCl_3$) matched identically with the ^{1}H NMR of the starting material.

2-Mercaptophenol (105) was prepared from 2-aminophenol in 25 per cent yield according to the procedure in the literature:[102] bp 106 °C; IR spectrum no 1553 (neat) 3440 (br, OH), 2550 (m, SH) 1560, 1480, 1475, 1200, 750 cm^{-1}; ^{1}H NMR spectrum no 6917 ($CDCl_3$) δ 7.55-6.62 (m, 4H, ArH), 6.45 (s, 1H, OH), 3.04 (s, 1H, SH).

2-Hydroxyphenyl Methyl Sulfide (106). [128] A solution of 2-mercaptophenol (5.0g, 0.039 mol) in methanol (5.36 mL) was placed in a 50 mL three-necked round-bottomed flask equipped with a thermometer, reflux condenser and a magnetic stirrer. Sodium hydroxide (1.45 g, 0.0390 mol) was added and the mixture was heated on a water-bath until the sodium hydroxide had dissolved. Then the flask was placed in an ice-water bath. Methyl iodide (5.5g, 0.050 mol) was slowly added with stirring, and the mixture was heated under reflux for one hour. After evaporation of the

solvent, water was added until the sodium iodide had dissolved. The organic phase was separated and the aqueous phase was extracted twice with ether. The combined organic phases were dried over anhydrous sodium sulfate. The ether was removed under reduced pressure. Purification by distillation under reduced pressure (aspirator) yielded 4.16g (75.0%): bp 96-97 °C (lit[128] 90-92 °C (10 torr)); IR spectrum no 2514 (neat) 3420 (br, OH) 1580, 1470, 1290, 1240, 1200 and 750 cm^{-1} ; ^1H NMR spectrum no 6923 ($CDCl_3$) δ 7.69 (m, 5H, ArH, OH), 2.28 (S, 3H, CH_3).

2'-Methylthiophenyl 4-Toluenesulfonate (107). [103]

2-Hydroxyphenyl methyl sulfide (1.4g, 0.010 mol) was dissolved in dichloromethane (20 mL) in a 50 mL round-bottomed flask equipped with a magnetic stirrer. The flask was placed in an ice-bath and triethylamine (1.01g, 0.0100 mol) was added with stirring. Then 4-toluenesulfonyl chloride (1.905g, 0.0100 mol) was added. The reaction mixture was stirred for fifteen hours. The mixture was washed with water (50 mL). The organic layer was dried over anhydrous magnesium sulfate, and concentrated under reduced pressure to give a white solid. Recrystallization from 95% ethanol gave 1.93g (67.7%): mp 66-68 °C; IR spectrum no 2535 (KBr) 1360 and 1170 cm^{-1} (s, SO_2); ^1H NMR spectrum no 6928 ($CDCl_3$) δ 8.00-7.80 and 7.5-7.2 (m, 8H, ArH), 2.42 (s, 3H, SCH_3), 2.30 (s, 3H, CH_3); ^{13}C NMR spectrum no 7288 ($CDCl_3$) δ 146.7,

145.3, 133.0, 129.6, 128.6, 127.3, 125.7, 122.3, 75.5 and 21.7; Anal. Calcd for $C_{14}H_{14}O_3S_2$: C, 57.12; H, 4.79. Found: C, 57.06; H, 4.76.

2'-Methylsulfonylphenyl 4-Toluenesulfonate (108). 2'-Methylthiophenyl 4-toluenesulfonate (6.49g, 0.022 mol) was dissolved in acetic acid (150 mL) in a 250 mL round-bottomed flask equipped with a magnetic stirrer. A solution of 30% hydrogen peroxide (9.46 mL, 0.110 mol) in acetic acid (25 mL) was added. The mixture was stirred for four days at room temperature. Then it was poured into water. The water mixture was extracted several times with chloroform. The combined chloroform extracts were washed with water until neutral, dried over anhydrous sodium sulfate, and concentrated under reduced pressure to yield a white solid. Recrystallization from 95% ethanol gave 5.5g (75%) of product: mp 114-115 °C; IR spectrum no 2537 (KBr) 1480, 1370, 1315, 1215, 1175, 860, and 720 cm^{-1}; ^1H NMR spectrum no 7045 ($CDCl_3$) δ 8.20-7.25 (m, 8H, ArH), 3.15 (s, 3H, CH_3), 2.24 (s, 3H, CH_3); ^{13}C NMR spectrum no 4778 ($CDCl_3$) δ 140.2, 135.2, 130.3, 129.9, 129.0, 128.8, 126.0, 121.8, 45.8 and 21.7. Anal. Calcd for $C_{14}H_{14}O_5S_2$: C, 51.53; H, 4.29. Found: C, 51.75; H, 4.34.

Reaction of 2'-Methylsulfonylphenyl 4-Toluene sulfonate with Sodium Hydride. Sodium hydride (0.30g, 75 mmol) was placed in flame-dried three-necked round-bottomed flask equipped with a magnetic stirrer. The flask was

capped with rubber septums and was flushed with nitrogen. By using a syringe, the sodium hydride was washed five times with dry ether or hexane. Dry THF (5 mL) was next added to the flask. The mixture was cooled to - 78 °C using a Dry ice-acetone bath. A solution of 2'-methylsulfonylphenyl 4-toluene sulfonate (0.50g, 15 mmol) in dry THF (20 mL) was made under nitrogen and then added to the sodium hydride by a syringe. After two hours at -78 °C, no reaction had occured (TLC). The mixture was allowed to warm to room temperature. After twelve hours at room temperature, water was added to the milky mixtue to destroy unreacted sodium hydride. The precipitate was filtered. THF was removed under reduced pressure and the majority of the residue was dissolved in dichloromethane. Some undissolved material was removed by filtration. The dichloromethane solution was dried over anhydrous magnesium sulfate and was then concentrated under reduced pressure to yield starting material which was identified by TLC, 0.0125g (2.46%).

The precipitate, which had been filtered after water had been added to the reaction mixture, was air dried: IR spectrum no 2678 (KBr) 3480, 3380, 1240-1180 (br,s), 1165, 1150 cm^{-1}; ^1H NMR spectrum no 7085 (D_2O) δ 7.85-7.25 (AA'BB', 4H, ArH), 2.35 (s, 3H, CH_3). The compound was identified as sodium 4-toluenesulfonate by nmr spectroscopy. The ^1H NMR of this compound was run, some commercial sodium 4-toluene sulfonate was added, and the

spectrum was recorded again. The bands in the second spectrum were more intense than in the first spectrum but at the same frequency. (spectrum no 7284)

The material insoluble in dichloromethane was dissolved in water, the solution was acidified with hydrochloric acid, and then the mixture was extracted with chloroform. After being dried over anhydrous magnesium sulfate, the chloroform was removed under reduced pressure to give a solid; 0.20g (75%) which was purified by colum chromatography (silca gel, ethyl acetate): mp 80-81 ^{o}C (lit[130] 80-83 ^{o}C); IR spectrum no 5070 (KBr) 3500 (br, OH), 1280 and 1120 cm^{-1} (s, SO_2); ^{1}H NMR spectrum no 7129 ($CDCl_3$) δ 8.90 (s, 1H, OH), 7.90-6.90 (m, 4H, ArH), 3.12 (s, 3H, CH_3); ^{13}C NMR spectrum no 7370 ($CDCl_3$) δ 155.6, 136.3, 128.5, 122.9, 120.6, 118.9 and 44.7. The compound was identified as 2-(methylsulfonyl)phenol (110) by comparison of the melting point and the spectra with those in the literature.[130]

2-Nitrobenzyl Bromide (113). [105,106]

2-Nitrotoluene (100g, 0.729 mol), N-bromosuccinimide (129g, 0.729 mol), dibenzoylperoxide (0.75g, 30 mmol) and carbon tetrachloride (175 mL) were heated at reflux for eighteen hours in a 250 mL round-bottomed flask. The reaction mixture was cooled to 5 ^{o}C, the precipitate of succinimide and N-bromosuccinimide was removed by filtration, and the carbon tetrachloride was removed under

reduced pressure. The dark brown residue was washed with 15% aqueous sodium bisulfite, water, 15% aqueous ferrous sulfate, and water. The organic layer was then dried over anhydrous sodium sulfate and was treated with charcoal. Unreacted 2-nitrotoluene was removed by distillation (bp 65 °C, 0.2 mm); the undistilled residue was recrystallized from warm low boiling point petroleum ether to give 15.0g (14.8%): mp 44-46 °C (lit[129] 45-48 °C); IR spectrum no 5276 (Nujol) 1445 (m), 1470 (S), 1390 cm (M); ^{1}H NMR spectrum no 7116 ($CDCl_3$) δ 8.20-7.30 (m, 4H, ArH), 4.85 (s, 2H, CH_2).

N-Methyl 4-toluenesulfonamide (114).[108]

4-Toluenesulfonyl chloride (95.3g, 0.500 mol) was divided into 3 portions of 60.0, 28.4 and a 6.90g. A solution sodium hydroxide (22g) in water (22 mL) was prepared with cooling. The 60g portion of sulfonyl chloride was added with swirling during about five min to 40% aqueous methylamine (54.7 mL, 0.600 mol) contained in a 500 mL round-bottomed flask. The mixture was allowed to heat up to 80-90 °C in order to maintain the sulfonamide, which form as an oil, in a molten condition (lit[105] mp 78 °C). After all of this portion of sulfonyl chloride had been added, the mixture was shaken vigorously. Boiling was prevented by mild external cooling with water in order to avoid an excessive loss of methylamine. As soon as the mixture had become acidic, as indicated by testing a drop on litmus paper, 50% sodium hydroxide solution (15.7 mL)

was added carefully with swirling. This was followed immediately by gradual addition of the 28.4g portion of the sulfonyl chloride as before. When the mixture had again become acidic, sodium hydroxide solution (7.8 mL) was added followed by the final 6.9g of the sulfonyl chloride . After the mixture had again become acidic, the remainder of the sodium hydroxide solution was added. The aqueous phase of the final mixture was alkaline. After the walls of the flask had been rinsed with a little water, the reaction was completed by heating the mixture, which consisted of two layers and a precipitate of sodium chloride, on a steam bath for fifteen minutes with vigorous stirring. The sodium chloride precipitate was filtered and washed once with ether. The filtrate was allowed to cool whereupon the product solidified and was filtered and washed with cold water to give 91.2g (98.9%). Recrystallization was achieved by dissolving the product in hot ether and then adding an equal amount of petroleum ether (low boiling point): mp 74-75 ^{o}C (lit[108] 76-79 ^{o}C); IR spectrum no 4940 (KBr) 3290 (s, N-H), 1325 and 1160 cm^{-1} (s, SO_2); ^{1}H NMR spectrum no 7513 ($CDCl_3$); δ 7.95-7.96 and 7.49-7.20 (AA'BB' ,4H, ArH). 4.85 (br, 1H, NH), 2.62 (s, 3H, CH_3), 2.42(s, 3H, CH_3).

N-Methyl-N-(2'-nitrobenzyl)-4-toluenesulfonamide (115). [107] N-Methyl-4-toluenesulfonamide (8.5g, .059 mol) and potassium hydroxide powder (5.0g, .058 mol) were placed in a 100 mL round-bottomed flask equipped with a

magnetic stirrer. The mixture was made into a paste by adding a small amount of 95% ethanol. A solution of 2-nitrobenzyl bromide (7.26g, .0390 mol) in 95% ethanol was added. The mixture was heated under reflux for fifteen min, then allowed to cool to room temperature. The inorganic salt was filtered. The ethanol was removed under reduced pressure to give a solid yellow residue which was then dissolved in chloroform. The solution was washed once with water, dried over anhydrous magnesium sulfate, and the chloroform removed under reduced pressure to yield 10.35g (82.00%) of a solid: mp 118-119 °C (ethanol); IR spectrum no 2768 (KBr) 1530 (s, NO_2), 1350 and 1170 (s, SO_2), 930, 770 and 550 cm^{-1}; ^1H NMR spectrum no 7357 ($CDCl_3$) δ 8.20-7.30 (m, 8H, ArH), 4.60 (s, 2H, CH_2), 2.75 (s, 3H, CH_3), 2.49 (s. 3H, CH_3); ^{13}C NMR spectrum no 0321 ($CDCL_3$) δ 146.9, 143.9, 134.4, 133.8, 132.2, 129.9, 129.6, 128.4, 127.3, 124.9, 51.1, 35.8 and 21.5. Anal. Calcd for $C_{15}H_{16}N_2O_4S$: C, 56.24; H, 5.04; N, 8.74. Found: C, 56.00; H, 5.08; N, 8.82.

This general method was used to prepare the following compounds.

<u>N-Methyl-N-(4'-nitrobenzyl)-4-toluenesulfonamide</u> was prepared in 75.5 per cent yield: mp 125-128 °C; IR spectrum no 4965 (KBr) 1515 and 1350 (s, NO_2), 1340 and 1160 cm^{-1} (s, SO_2); ^1H NMR spectrum no 7863 δ ($CDCl_3$) δ 8.45-7.10 (s, 8H, ArH), 4.28 (s, 2H,

CH_2), 2.65 (s, 3H, N-CH_3), 2.48 (s, 3H, CH_3); ^{13}C NMR spectrum no 7305 ($CDCl_3$) δ 147.6, 145.9, 145.5, 134.0, 129.8, 128.8, 127.5, 125.8, 55.5, 54.8 and 21.5. Anal. Calcd. $C_{15}H_{16}N_2O_4S$: C, 56.24; H, 5.04; N, 8.74. Found: C, 56.24; H, 5.02; N, 8.75.

N-Methyl-N-(3'-nitrobenzyl)-4-toluenesulfonamide was prepared in 74 per cent yield: mp 104-105 °C; IR spectrum no 5116 (KBr) 1540 and 1360 (s, NO_2), 1340 and 1160 cm^{-1} (s, SO_2); ^1H NMR spectrum no 7961 ($CDCl_3$) δ 8.38-7.30 (s, 8H, ArH) 4.28 (s, 2H, CH_2), 2.65 (s, 3H, N-CH_3), 2.48 (s, 3H, CH_3); ^{13}C NMR spectrum no 5592 ($CDCl_3$) δ 148.4, 145.9, 138.2, 134.2, 134.0, 129.9, 129.8, 127.3, 122.9, 55.4, 54.8, and 21.5. Anal. Calcd for $C_{15}H_{16}N_2O_4S$: C, 56.24; H, 5.04; N, 8.74. Found: C, 55.85; H, 4.98; N, 8.72.

N-Benzyl-N-methyl-4-toluenesulfonamide (126) was prepared in 83.2 per cent yield: mp 93-94 °C; IR spectrum no 5098 (KBr) 1345 and 1170 cm^{-1} (s, SO_2); ^1H NMR spectrum no 7927 ($CDCl_3$) δ 7.95-7.68, 7.55-7.18 (m, 8H, ArH), 4.15 (s, 2H, CH_2), 2.58 (s, 3H, N-CH_3), 2.46 (s, 3H, CH_3); ^{13}C NMR spectrum no 5472 ($CDCl_3$), δ 143.4, 135.7, 134.4, 129.7, 128.5, 128.3, 127.8, 127.4, 54.1, 34.3, and 21.5. Anal. Calcd for: $C_{15}H_{17}NO_2S$: C, 65.67; H, 6.25; N, 5.11. Found: C, 65.08: H, 6.30; N, 4.99.

N-Methyl-N-(2'-bromobenzyl)-4-toluenesulfonamide (131) was prepared in quantitative yield: mp 82-83 °C;

IR spectrum no 5278 (KBr) 1350 and 1165 cm^{-1} (s, SO_2); ^1H NMR spectrum no 10579 ($CDCl_3$) δ 7.92-7.05 (m, 4H, ArH), 4.28 (s, 2H, CH_2), 2.65 (s, 3H, $N-CH_3$), 2.42 (s, 3H, CH_3); ^{13}C NMR spectrum no 7582 ($CDCl_3$) δ 143.6, 135.0, 134.4, 132.7, 129.8, 129.2, 127.9, 127.5, 125.4, 53.6, 35.0, and 21.5, Anal. Calcd for $C_{15}H_{16}BrNO_2S$: C, 50.86; H, 4.55; N, 3.95. Found: C, 51.24; H, 4.63; N, 4.00.

N-Methyl-N-(2'-aminobenzyl)-4-toluenesulfonamide (116). [109]

Method A ; N-Methyl-N-(2'-nitrobenzyl)-4-toluenesulfonamide (0.50g, 1.5 mmol) was added to granulated tin (1g) in a 50 mL three-necked round-bottomed flask equipped with a mechanical stirrer and a reflux condenser. Some 95% ethanol (2.5 mL) was added to help facilitate the reduction. Hydrochloric acid (10%, 10 mL) was added slowly with vigorous stirring. Next, the mixture was heated to boiling for twenty min. Then the mixture was decanted while it was still hot into water (5 mL). Sufficient 5.0 N sodium hydroxide solution was added to dissolve the tin hydroxide. The aqueous solution was extracted three times with ether. The combined extracts were dried over anhydrous magnesium sulfate, and concentrated on a rotary evaporator to give a yellow solid: Recrystallization from ethanol gave 0.225g (50.0%).

Method B ; N-Methyl-N-(2'-nitrobenzyl)-4-toluenesulfonamide (2.08g, 6.50 mmol) and 95% ethanol (175

mL) were placed in a 250-mL round-bottomed flask equipped with a magnetic stirrer. A solution of stannous chloride (5.50g, 0.0255 mol) in concentrated hydrochloric acid (10 mL) was added with stirring. The mixture was heated under reflux for three hours at which time no starting material was detected by TLC (95% $CHCl_3$, 5% EtOAc). The solution was allowed to cool to room temperature. Then it was made basic with 5.5N NaOH after which it was extracted three times with ether. The combined extracts were washed with water, dried over anhydrous magnesium sulfate and concentrated to give a white solid; 1.70g (80%): mp 121-122 ^{o}C; IR spectrum no 2771 (KBr) 3490 and 3400 (s, NH_2), 1235 and 1160 cm^{-1} (S, SO_2); ^{1}H NMR spectrum no 7353 ($CDCl_3$) δ 7.90-7.43 (m, 8H, ArH) 4.40 (br, 2H, NH_2), 3.93 (s, 2H, CH_2), 2,55 (s, 3H, CH_3), 2.41 (s, 3H, CH_3); ^{13}C NMR spectrum no 4965 ($CDCl_3$) δ 146.5, 133.2, 131.1, 129.8, 129.7, 127.7, 117.9, 117.3, 115.9, 52.0, 34.0 and 21.5. Anal. Calcd for $C_{15}H_{18}N_2O_2S$: C, 62.04; N, 9.65; H, 6.25. Found: C, 62.37; N, 9.55; H, 6.36.

The following compounds were prepared by method A.

N-Methyl-N-(4'-aminobenzyl)-4-toluenesulfonamide (124) was separated from the crude solid product by Soxhlet extraction (ether-solvent) in 75.5 per cent yield: mp 153-154 ^{o}C; IR spectrum no 3097 (KBr) 3000 and 3410 (s, NH_2), 1355 and 1155 cm^{-1} (s, SO_2); ^{1}H NMR spectrum no 7895, ($CDCl_3$) δ 7.95-7.69, 7.65-7.00 and

6.85-6.60 (AA'BB', 8H, ArH), 4.02 (s, 2H, NH_2), 3.65 (s, 2H, CH_2), 2.56 (s, 3H, N-CH_3), 2.45 (s, 3H, CH_3); ^{13}C NMR spectrum no 5480 ($CDCl_3$) δ 146.2, 143.2, 134.4, 129.6 127.4, 125.0, 115.0, 55.7, 55.9 and 22.1. Anal. Calcd for $C_{15}H_{18}N_2O_2S$: C, 62.04; H, 6.25; N, 9.65; Found: C, 61.70: H, 6.31; N, 9.56.

N-Methyl-N-(3'-aminobenzyl)-4-toluenesulfonamide (125) was separated from the crude solid product by Soxhlet extraction in 52.2 per cent yield: mp 112-113 °C; IR spectrum no 5115 (KBr) 3000 and 3410 (s, NH_2), 1335 and 1160 cm^{-1} (s, SO_2); ^1H NMR spectrum no 7965 ($CDCl_3$) δ 7.92-6.48 (m, 8H, ArH), 4.05 (s, 2H, CH_2), 3.70 (br, 2H, NH_2), 2.60 (s, 3H, N-CH_3), 2.45 (s, 3H, CH_3); ^{13}C NMR spectrum no 5540 ($CDCl_3$) δ 146.9, 143.3, 136.9, 134.4, 129.7, 129.4, 127.5, 118.4, 114.6, 54.1, 54.4 and 21.5. Anal. Calcd for $C_{15}H_{18}N_2O_2S$: C, 62.04; H, 6.25; N, 9.65. Found: C, 62.06; H, 6.38; N, 9.75.

N-Methyl-N-(4-dimethylamino)benzylimine [132]

Methylamine (40% aqueous solution, 7.75 mL) was added to a solution of 4-dimethylaminobenzaldehyde (10g, 0.067 mol) in methanol. The solution was stirred overnight at room temperature, poured into saturated brine (50 mL), and then extracted with five 25 mL portion of chloroform. The combined extracts were dried over anhydrous magnesium sulfate. The solvent was taken off under reduced pressure

to yield a yellow solid 10.5g (95.7%) which was used without purification: ^{1}H NMR no 8599 ($CDCl_3$) δ 8.17 (s, 1H, CH), 7.75-7.45 and 6.85-6.60 (AA'BB', 4H, ArH), 3.45 (s, 3H, N-CH_3), 3.00 (s, 6H, $N(CH_3)_2$); ^{13}C NMR spectrum no 6110 ($CDCl_3$) δ 162.2, 151.9, 129.1, 124.5, 115.5, 47.9 and 40.1.

N-Methyl-N-(4-dimethylamino)benzylamine.[132] 4-Dimethylamino- N-methylbenzylimine (3.8g, 0.023 mol), dry methanol (379 mL) and sodium borohydride (0.87g, 0.023 mol) in a 500 mL round-bottomed flask were stirred at room temperature for eleven hours. The solution was poured into a mixture of ethyl acetate (300 mL) and saturated potassium carbonate (30 mL). The aqueous layer was extracted four times with ethyl acetate (100 mL). The combined extracts were dried over anhydrous magnesium sulfate. The solvent was evaporated under reduced pressure to yield a yellow liquid which was used in the next reaction without further purification: IR spectrum no 4204 (neat) 3340 (br, NH), 1160, 1515 and 1340 cm^{-1}; ^{1}H NMR spectrum no 885 ($CDCl_3$) δ 7.38-7.02 and 6.88-6.25 (AA'BB' , 4H, ArH), 3.60 (s, 2H, CH_2), 2.90 (s, 7H, $N(Me)_2$ and NH), 2.35 (s, 3H, N-CH_3).

N-Methyl-N-(4'-dimethylaminobenzyl)-4-toluenesulfonamide (127). N-Methyl-4-dimethylaminobenzylamine (2.0g, .012 mol) in dichloromethane (20 mL) in a 50 mL round bottomed-flask was cooled in an ice-salt bath. Pyridine (1

mL) and then 4-toluenesulfonyl chloride (1.9g, 0.012 mol) were added. After two hours, the reaction was complete (TLC). The reaction mixture was poured into water (20 mL). The organic layer was separated and washed once with water (15 mL), dried over anhydrous magnesium sulfate and concentrated under reduced pressure to give an orange solid. Recrystallization from 95% ethanol gave 2.48g (63.9%): mp 130-131 °C; IR spectrum no 5747 (KBr) 1335 and 1165 cm^{-1} (S, SO_2); ^1H NMR spectrum no 6695 ($CDCl_3$) δ 7.89-7.62, 7.62-7.00 and 6.81-6.65 (AA'BB', 8H, ArH), 4.02 (s, 2H, CH_2), 2.99 (s, 6H, $N(Me)_2$), 2.55 (s, 3H, $N-CH_3$), 2.45 (s, 3H, CH_3); ^{13}C NMR spectrum no 6144 ($CDCl_3$) δ 150.2, 143.1, 134.5, 129.5, 127.5, 125.0, 112.5, 55.0, 40.5, 39.8 and 21.4. Anal. Calcd for $C_{17}H_{22}N_2O_2S$: C, 64.12; H, 6.96; N, 8.80. Found: C, 63.07; H, 7.09; N, 8.58.

Reaction of N-methyl-N-(2'-aminobenzyl)-4-toluenesulfonamide with n-Butyllithium. N-Methyl-N-(2'-aminobenzyl)-4-toluenesulfonamide (0.20g, 0.69mmol) was placed in an oven-dried 50 mL three-necked round-bottomed flask equipped with a magnetic stirrer. The flask was flushed with nitrogen and placed in an ice-bath. Dry THF (15 mL) and then 1.3 M n-butyllithium (2.12 mL, 2.76 mmol) were added. The reaction was followed by TLC ($CHCl_3$:EtOAc). The reaction solution turned dark-red a few minutes after adding the n-butyllithium. After seven hours (no change in TLC) five drops of water were added.

The reaction mixture was stirred for fifteen more min. A white precipitate was filtered and the solvent was removed using a rotary evaporator. The residue was dissolved in ether. The organic layer was washed with water, dried over anhydrous magnesium sulfate, and concentrated on the rotary evaporator to yield a yellow oil. TLC in hexane: ether showed six spots. Preparative TLC was used for separation. Only 2 bands on the preparative plate could be separated and identified (A, B).

A. R_f 0.3 (ether:Hexane), white solid .048g (25%); ^1H NMR, IR, mp and mixed mp were identical with N-methyl- 4-toluenesulfonamide.

B. R_f 1.3 (ether:hexane), thick oil; .0253g (15%): IR spectrum no 2803 (neat) 3400 and 3370 (s, NH_2) 2980-2870 cm^{-1} (s, aliphatic CH); ^1H NMR spectrum no 7588 ($CDCl_3$) δ 7.3-6.59 (m, 4H, ArH) 3.58 (br, 2H, NH_2), 2.52 (t, 2H, CH_2), 1.85-0.65 (m, 9H, n-Bu); ^{13}C NMR spectrum no 7391 ($CDCl_3$) δ 144.0, 129.4, 127.0 126.8, 118.7, 115.5, 31.9, 31.2, 28.4, 22.6 and 14.0; MS no 404 M/e (rel intensity) 163 (287, M^+), 164 (39, M+1), 162 (16, M-1), 107 (108), 106 (1000), 77 (119). The compound was identified as 2-pentylaniline (119) from the above spectra.

If the reaction was stopped 1 hour after adding the n-butyllitnium by adding methyl iodide, product A was found along with C and D. C (11.2%): IR spectrum no 3103 (neat) 2980, 2800 and 2780 cm^{-1}; ^1H NMR spectrum no 7801

($CDCl_3$) 7.45-7.00 (m, 4H, ArH), 2.61 (s, 8H, $N(CH_3)_2$ and CH_2) 1.85-0.05 (m, 9H, n-Bu); ^{13}C NMR spectrum no 5402 ($CDCl_3$) 152.69, 137.67, 129.48, 126.22, 125.23, 119.26, 45.15, 32.00, 30.56, 30.50, 22.63 and 14.0. This compound was identified as 2-pentyl-N,N-dimethylaniline. D was a white solid: mp 104-105 °C; IR spectrum no 2855 (KBr) 1345 and 1165 cm^{-1} (s, SO_2); ^1H NMR spectrum no 7584 ($CDCl_3$) δ 7.92-7.01 (m, 8H, ArH) 4.51 (s, 2H, CH_2), 2.60 (s, 6H, $N(CH_3)_2$), 2.53 (s, 3H, N-CH_3), 2.46 (s, 3H, CH_3); ^{13}C NMR spectrum no 5179 ($CDCl_3$) δ 143.2, 134.9, 129.9, 129.7, 129.2, 128.1, 127.5, 125.6, 119.1, 48.9, 45.1, 34.5 and 21.5. This compound is identified as N-Methyl-N-(2'-N',N'-dimethyl benzyl)-4-toluenesulfonamide (123) from the above spectra.

This general procedure was used for the following reaction.

<u>Reaction of N-methyl-N-benzyl-4-toluenesulfonamide with n-Butyllithium.</u> The procedure was the same as above, except that a white precipitate was obtained after the n-butyllithium was added. The reaction was complete in one hour (TLC). Four drops of water were added. The precipitate was filtered and the filtrate was worked up as usual. Three compounds were indicated by TLC of the filtrate. They were separated by preparative TLC. The major band was an oily liquid, 0.0805g (25.0%): IR spectrum no 5103 (neat) 2980-2780 (s, aliphatic CH), 3320 cm^{-1} (br, NH); ^1H

NMR spectrum no 7950 ($CDCl_3$) δ 7.34 (m, 5H, ArH), 3.45 (t, 1H, CH), 2.26 (s, 3H, N-CH_3), 2.05 (br, 1H, NH), 1.80-0.80 (m, 9H, n Bu); ^{13}C NMR spectrum no 7671 ($CDCl_3$) δ 144.2, 128.3, 127.2, 126.8, 65.6, 57.7, 34.3, 28.6, 22.7 and 13.9; MS no 420 M/e (rel intensity) 177 (40, M^+) 176 (61, M-1) 121 (551), 120 (1000). The compound was identified as 1-methylamino-1-phenyl pentane (129) from the above spectra. The white precipitate was identified as lithium 4-toluenesulfinate. Its IR and NMR spectra matched those in the literature. An ^1H NMR was also run in which authentic sodium 4-toluenesulfinate was added to the unknown. An increase in the intensity of the spectrum occured, but no new peaks were observed.(^1H NMR spectrum no 7726)

Reaction of N-methyl-N-(3'-aminobenzyl)-4-toluene sulfonamide with n-Butyllitnium. The procedure was the same as above except that the solution turned dark green forty min after adding the n-butyllithium. TLC ($CHCl_3$ and MeOH) showed ten spots. None of them were separated or identified.

Reaction of N-methyl-N-(4'-aminobezyl)-4-toluene sulfonamide with n-Butyllithium. The procedure was the same as above. TLC ($CHCl_3$) showed more than 6 spots. Only 2 were separated by preparative TLC. One product (0.0695g, 21.7%) was identified as N-methyl 4-toluenesulfonamide. The mp and spectra agreed with published data (Sadtler Spectrum 8085 (NMR), 6860 (IR)).

The other compound was an oily liquid (0.0550g, 11.8%): IR spectrum no 5104 (neat) 3480 and 3380 cm^{-1} (s, NH_2); ^1H NMR spectrum no 7941 ($CDCl_3$) δ 7.10-6.9 and 6.8-6.55 (AA'BB', 4H, ArH), 3.52 (br, 2H, NH_2), 2.68-2.51 (t, 2H, CH_2), 1.80-0.65 (m, 9H, n-Bu); MS no 425 M/e (rel intensity) 163 (178, M^+), 164 (54, M+1), 107 (200), 108 (1000). The compound was identified as 4-pentylaniline (128) from the above spectra.

Reaction of N-methyl-N-(4'-dimethylaminobenzyl)-4-toluenesulfonamide with n-Butyllithium. The procedure was the same as above. Two products were isolated. One was a solid; (0.189g, 76.9%) which was identified as lithium 4-toluenesulfinate. Its spectral data agreed with published spectra (Sadtler Spectrum 4457 (NMR), 13486 (IR)). The other product was a semi-solid (0.0478g, 24.0%): IR spectrum no 5828 (neat) 2970, 2940, 2860, 2800 (s. aliphatic CH); ^1H NMR spectrum no 8794 ($CDCl_3$) δ 7.38-7.02 and 6.89-6.60 (AA'BB', 4H, ArH), 3.40 (t, 1H, CH), 2.95 (s, 6, $N(Me)_2$), 1.91-0.65 (m, 9H, n-Bu); ^{13}C NMR spectrum no 7770 ($CDCl_3$) δ 149.0, 127.9, 127.3, 111.5, 65.5, 59.5, 35.3, 27.5, 21.5 and 12.9; MS no 470 M/e 220 (47, M^+), 189 (218) 163 (1000), 160 (537). It was identified as 1-methylamino-1-(N,N-dimethyl aminophenyl) pentane (130) from the above spectra.

Reaction of N-methyl-N-(2'-bromobenzyl)-4-toluenesulfonamide with n-Butyllithium. The procedure was the same as above. More than six spots were found by

TLC. No isolation was attempted.

Attempted Synthesis of 2-Oxy-3H-1,2,3-benzoxathiazole (135). o-Aminophenol (1.09g., 0.0100 mol) was dissolved in anhydrous diethyl ether (25 mL) in a 100 mL three-necked round-bottomed flask equipped with a magnetic stirrer and an addition funnel. The flask was capped with a septum, flushed with nitrogen, and placed in an ice bath. Triethylamine (2.02g, 0.0200 mol) was added with stirring. Thionyl chloride (1.19g, 0.0100 mol) in anhydrous diethyl ether (5 mL) was added dropwise. The mixture was black after twenty min. After one hour a precipitate was filtered. The filtrate was concentrate under reduced pressure to give a brownish oil. After kugelrohr distillation of the brownish oil, only starting material was recovered.

N-(2'-Hydroxyphenyl)-4-toluenesulfonamide (141).[1] o-Aminophenol (1.09g, 0.0100 mol) was suspended in dichloromethane (20 mL) in a 50 mL round-bottomed flask provided with a magnetic stirrer. The flask was placed in a Dry Ice-acetone bath and the suspension was stirred. Pyridine (1 mL, 0.01 mol) was added followed by 4-toluenesulfonyl chloride (1.91 g, 0.0100 mol). The mixture was stirred for one hour at room temperature. Then the solution was washed with water (10 mL). The methylene chloride layer was dried over anhydrous magnesium sulfate and then concentrated under reduced pressure to give 2.24g (85.0%): mp 138-139 ^{o}C (toluene); IR spectrum no 1829

(KBr) 3410 (s, OH), 3290 (s, NH), 1315 and 1155 (s, SO_2), 1405, 1285, 1080, 750 and 670 cm^{-1}; ^1H NMR spectrum no 8729 ($CDCl_3$) δ 7.80-6.50 (m, 10H, ArH, NH, OH), 2.35 (S, 3H, CH_3).

3-Tosyl-1,2,3-benzoxathiazole-2-oxide (142).[113] N-(2-Hydroxy phenyl)-4-toluenesulfonamide (2.00g, 7.00 mmol), thionyl chloride (2.0 mL, 28 mmol) and benzene (30 mL) were placed in a 100 mL round-bottomed flask. The reaction mixture was heated under reflux for one and a half hours after which the solvent was removed under reduced pressure. Trituration of the residue with ether (10 mL) gave 2.03g (87.2%): mp 130-131 °C (EtOAc), (lit[113] mp 132 °C); IR spectrum no 3271 (KBr) 1355 and 1165 (s, SO_2), 1215 (s, SO), 870, 815, 685 cm^{-1}; ^1H NMR spectrum no 8780 ($CDCl_3$) δ 8.00-7.75 and 7.50-7.05 (m, 8H, ArH), 2.38 (s, 3H, CH_3); ^{13}C NMR spectrum no 6246 ($CDCl_3$) δ 148.3, 145.8, 134.3, 130.1, 127.7, 125.5, 124.6, 114.9, 113.3 and 21.5.

Attempted Oxidation of 3-Tosyl-1,2,3-benzoxathiazole -2-oxide. 3-Tosyl-1,2,3-benzoxathiazole-2-oxide (1.9g, 5.0 mmol) was dissolved in acetic acid (15 mL) in a 50 mL round-bottomed flask equipped with a magnetic stirrer. The flask was placed in an ice bath and stirring was begun. Potassium permanganate (0.46g., 3.0 mmol) in water (5 mL) was added and the mixture was stirred until the color of potassium permanganate persisted. The reaction mixture was poured into cold sodium carbonate solution (2.12g in 5 mL

of water). Then a saturated solution of sodium bisulfite was added to decolorize the mixture. The solution was extracted with ether five times. The combined ether layers were dried over anhydrous magnesium sulfate. The ether was removed under reduced pressure, only starting material was recovered.

5-Tosyl-1,2,5-benzoxathiazole-2,2-dioxide (145).

Method A : 5-Tosyl-1,2,5-benzoxathiazole-2-oxide (0.927g, 2.70 mmol) in dry chloroform (50 mL) was placed in a 200 mL round-bottomed flask equipped with a magnetic stirrer and an addition funnel. The flask was placed in an ice bath. m-Chloroperbenzoic acid (0.52g, 5.0 mmol) in dry chloroform (45 mL) was added dropwise with stirring. The solution was stirred for eleven hours with the temperature less than 10 ^{o}C. The solution was neutralized by passing it through a basic alumina column. The solvent was removed under reduced pressure to give a light yellow solid which was purified by silica column chromatograpny to give 0.44g (45%) of white solid, mp 120 °C (decomposition).

Method B :[114] N-(2'-Hydroxyphenyl)-4-toluenesulfon amide (9.0g, 0.034 mol) was dissolved in dichloromethane (100 mL), freshly distilled from calcium hydride, in a 100 mL three-necked round-bottomed flask equipped with a mechanical stirrer and an addition funnel. The flask was flushed with nitrogen and placed in a Dry Ice-acetone bath. Triethylamine (9.48 mL, 0.0680 mol) in dichloromethane (10 mL) was added with stirring. Then freshly distilled

sulfuryl chloride (4.59g, 2.73 mL, .0340 mol) in dichloromethane (10 mL) was added dropwise with rapid stirring over a thirty min period. The mixture, which was cloudy, was kept at -78 °C with rapid stirring for fifteen min; then it was allowed to warm to 5 °C. Addition of water (50 mL) produced two clear phases; the aqueous phase was washed with dichloromethane (20 mL). The combined organic phases were washed three times with water, dried over anhydrous magnesium sulfate, and then the solvent was removed under reduced pressure to give a light yellow solid. Purification by column chromatography (silica, $CHCl_3$) a white solid; 9.50g (85.4%): mp 120 °C (decomposition); IR spectrum no 2112 (KBr) 1590 and 1180 (s, SO_2N), 1475, 1220 cm^{-1} (s, SO_2O); ^1H NMR spectrum no 0084 ($CDCl_3$) δ 8.07-7.03 (m, 8H, ArH), 2.38 (s, 3H, CH_3); ^{13}C NMR spectrum no 4291 ($CDCl_3$) δ 146.9, 141.1, 130.0, 128.7, 126.5, 125.9, 115.6, 111.9 and 21.7. Anal. Calcd for $C_{13}H_{11}NO_5S_2$: C, 48.00; H, 3.38; N, 4.31. Found: C, 48.02; H, 3.44; N, 4.28.

3-Tosyl-5-nitro-1,2,3-benzoxathiazole-2,2-dioxide (170) was synthesized as above using method B in 71.5 per cent yield: mp 117-118 °C (EtOH); IR spectrum no 5119 (KBr) 1540 and 1300 (s, NO_2), 1425, 1405, 1255 and 1185 cm^{-1} (s, SO_2); ^1H NMR spectrum no 16300 ($CDCl_3$) δ 8.5, 8.31-7.85 and 7.59-7.19 (m, 9H, ArH), 2.35, (s, 3H, CH_3); ^{13}C NMR spectrum no 7525

($CDCl_3$) δ 147.8, 144.8, 144.0, 132.1, 130.4, 128.8, 126.6, 121.8, 112.2, 110.2, and 21.8. Anal. Calcd for $C_{15}H_{10}N_2O_7S_2$: C, 42.16; H, 2.70; N, 7.57. Found: C, 41.94; H, 2.72; N, 7.51.

Phenyllithium. n-Butyllithium (9.8 mL, 0.57 mol) in hexane was divided in four and placed in four nitrogen-flushed septum-capped centrifuge tubes. Hexane (5 mL) was added to each tube. Bromobenzene (4.0g, 0.25 mol) was added to each tube. The mixtures were allowed to stand in an oil bath at 60 ^{o}C. After three hours, the oil bath was removed. The mixtures were centrifuged. The supernatant solvents were removed with a syringe and the remaining solids were washed with dry hexane. The centrifuging and washing processes were repeated several times. The combined solid product was stored in hexane under nitrogen.

Titration of Phenyllithium Solution. Bipyridyl (ca. 1 mg) was placed in a flame-dried round-bottomed flask equipped with a magnetic stirrer. Then the flask was capped with a rubber septum and flushed with nitrogen. A known volume of phenyllithium solution in hexane-ether was added to the flask by syringe. A red solution resulted. Then, the solution was titrated with sec-butyl alcohol to a sharp end point (red to yellow). The result of the titrations are given in table A.

Table A Results of PhLi titrations.

	PhLi(mL)	s-Butyl alcohol(mL)	conc.of PhLi(M)
1	4.60	1.00	0.348
2	4.60	1.80	0.391
3	4.80	1.60	0.333
		average	0.357

Reaction of 3-Tosyl-1,2,3-benzoxathiazole-2,2-dioxide with Phenyllithium. Phenyllithium solution (8.40 mL, 3.08 mmol) and THF (4.2 mL) were placed in an addition funnel equipped with a cooling jacket containing an ice-methanol mixture (-12 °C). This cooled solution was then added to a solution of 3-tosyl-1,2,3-benzoxathiazole-2,2-dioxide (0.500g, 1.54 mmol) in THF at -78 °C. The reaction mixture was stirred for forty min (dark red color) and then quenched with three drops of water. After fifteen min of being stirred, the white precipitate was filtered and the solvent was removed under reduced pressure. Dichloromethane was added to dissolve the brown residue. The mixture was washed once with water. The organic layer was dried over anhydrous magnesium sulfate and concentrated under reduced pressure to give 0.280g (77.7%) of a light yellow solid: mp 124-125 °C (EtOH); IR spectrum no 2125 (KBr) 1305 and 1155 cm^{-1} (s, SO_2); ^1H NMR spectrum no 6399 ($CDCl_3$) δ 8.10-7.25 (m, 9H, ArH), 2.39 (s, 3H, CH_3). The compound was identified as phenyl 4-tolyl sulfone (144) by comparison with spectra from an authentic sample.

N-(2'-Methoxyphenyl)-4-toluenesulfonamide (15b).

o-Anisidine (2.46g, 0.0200 mol) in dichloromethane (40 mL) was placed in 100 mL round-bottomed flask equipped with a magnetic stirrer. The flask was placed in an ice bath and the solution was stirred. Pyridine (2.0 ml, 0.020 mol) was added followed by 4-toluenesulfonyl chloride (3.81g, 0.0200 mol). The mixture was allowed to warm to room temperature. After two hours it was poured into water (20 mL) and the organic layer was separated. The water layer was extracted one more time with dichloromethane (10 mL). The combined organic layers were washed once with water and were dried over anhydrous magnesium sulfate. The dichloromethane was removed under reduced pressure and the solid residue was recrystallized from 95% ethanol to give 4.43g (80%) of white crystals: mp 122-123 ^{o}C; IR spectrum no 5749 (KBr) 3360 (s, NH), 1340 and 1160 (s, SO_2), 1260 and 1105 cm^{-1} (m, C-O); ^{1}H NMR Spectrum no 2059 ($CDCl_3$) δ 7.82-6.65 (m, 8H, ArH), 3.85 (s, 3H, CH_3), 2.35 (s, 3H, CH_3). Anal. Calcd for $C_{14}H_{15}NO_3S$: C, 60.60; H, 5.45; N, 5.05. Found: C, 60.42; H, 5.53; N, 5.00.

Reaction of 3-Tosyl-1,2,3-benzoxathiazole-2,2-dioxide with Hydrochloric acid. An attempted acidic hydrolysis of the title compound was followed by UV. A solution (EtOH) of the compound (1.54×10^{-4}) was scanned by the Cary 219 at 330-220 nm. Excess HCl solution was added to the sample cuvette. No change in absorbance occured. A similar

reaction was carried out on a large scale and monitored by TLC. No change was observed after three hours.

Reaction of 3-Tosyl-1,2,3-benzoxathiazole-2,2-dioxide with Sodium Hydroxide. A sample of the title compound (0.200g, 0.615 mmol) was dissolved in CH_3CN: EtOH (3:2 by volume). Excess sodium hydroxide solution (0.50 N) was added. The flask was stoppered, then shaken vigorously and allowed to stand at room temperature for three hours with occasional shaking. The reaction mixture was acidified with conc. HCl then extracted twice with chloroform. The combined extracts were dried over annydrous magnesium sulfate and concentrated under reduced pressure to give a brownish oil which was purified by preparative TLC (70% yield). The TLC, IR and NMR and of the compound matched those of N-(2'-hydroxyphenyl)-4-toluenesulfonamide (151).

Reaction of 3-Tosyl-1,2,3-benzoxathiazole-2,2-dioxide with Methylamine. 3-Tosyl-1,2,3-benzoxathiaxole -2,2-dioxide (.13g, 0.40 mmol) was dissolved in acetonitrile (10 mL) in a 25 mL round-bottomed flask equipped with a magnetic stirrer. Methylamine solution, 40% by weight (.0116g, .0290 mL, 0.400 mmol) was added and the solution was stirred overnight. The mixture was concentrated on a rotary evaporator. The residue was extracted with dichloromethane (10 mL) and washed once with water. The organic layer was dried over anhydrous magnesium sulfate. The solvent was removed under reduced pressure to give a white solid, 0.127g (88.9%). Recrystallization from

95% ethanol gave crystals: mp 121-122 °C; IR spectrum no 4763 (KBr) 3320 (s, NH) 1350, 1300, 1175 cm^{-1} (s, SO_2); ^1H NMR spectrum no 0917 ($CDCl_3$) δ 7.89-7.00 (m, 9H, ArH and NH), 5.27 (br, 1H, NH), 2.83 (d, 3H, NCH_3), 2.36 (s, 3H, CH_3); ^{13}C NMR spectrum no 0908 ($CDCl_3$) δ 144.2, 140.7, 135.9, 129.7, 127.5, 127.3, 125.7, 122.6, 30.5 and 21.5. Anal. Calcd for $C_{14}H_{16}N_2O_5S_2$: C, 47.18; H, 4.52; N, 7.85. Found: C, 47.05; H, 4.44; N, 7.81. This compound was identified as 2'-(N'-Tosyl)phenyl-N-methyl sulfamate (148a) by the above spectra and the analysis.

Reaction of 3-Tosyl-1,2,3-benzoxathiazole-2,2-dioxide with tert-Butylamine. The procedure was the same as used above. 2'-(N'-Tosyl)phenyl-N-tert-butyl sulfamate (148b)was obtained in 44 per cent yield: IR spectrum no 4902 (KBr) 3320 and 3280 (s, NH), 1335 and 1170 cm (s, SO_2); ^1H NMR spectrum no 7179 ($CDCl_3$) δ 7.76-7.12 (m, 9H, ArH and NH), 5.47 (s, 1H, NH), 2.34 (s, 3H, CH_3), 1.35 (s, 9H, $C(CH_3)_3$); ^{13}C NMR spectrum no 7198 ($CDCl_3$) δ 144.0, 140.8, 135.9, 129.9, 129.6, 127.3, 125.5, 123.1, 122.7, 50.2 and 21.5. Anal. Calcd for $C_{17}H_{22}N_2O_5S_2$: C, 51.24; H, 5.56; N, 7.03. Found: C, 50.95; H, 5.66; N, 6.99.

Reaction of 3-Tosyl-1,2,3-benzoxathiazole-2,2-dioxide with Sodium Methoxide. Sodium methoxide (0.20M) was prepared by adding sodium metal (0.092g) to absolute methanol (20 mL) under a nitrogen atmosphere. This solution

was kept under nitrogen. 3-Tosyl-1,2,3-benzoxathiazole-2,2-dioxide (.150g, 0.400 mmol) was dissolved in a 3:1 mixture (v/v) of methanol and acetonitride (12 mL) in a 25 ml round-bottomed flask equipped with a magnetic stirrer. The system was flushed wih nitrogen. Sodium methoxide solution (2.0 ml, 0.40 mmol) was then added. After being stirred for twelve hours at room temperature, the reaction was complete (TLC). Water (10 mL) was added. Acetonitrile and methanol were removed on a rotary evaporator. The remaining water layer was extracted three times with dichloromethane (5 mL). The combined extracts were dried over anhydrous magnesium sulfate and concentrated on a rotary evaporator to give a compound (.0251g, 33.7%) whose physical and spectral data agreed with those of methyl-4-toluenesulfonate (149). The water layer was acidified with 3M HCl. The water then was evaporated under reduced pressure to yield a white solid which was dissolved in acetone. The undissolved residue was removed by filtration. The acetone filtrate was dried over anhydrous magnesium sulfate. After removal of the acetone a white solid was obtained. TLC (ether:hexane) exhibited two spots. Preparative TLC (ether-hexane, 3:2) yielded two compounds. The physical and spectral data for one of these compounds (0.0093g, 8.4% yield) matched those of N-methyl-N- (2'-hydroxyphenyl)-4-toluenesulfonamide (150) while those of the other compound (.0585g, 56.5% yield) matched those of N-(2'-hydroxyphenyl)-4-toluenesulfonamide

(151).

Reaction of 3-Tosyl-1,2,3-benzoxathiazole-2,2-dioxide with Potassium tert-Butoxide. 3-Tosyl-1,2,3-benzoxathiazole -2,2-dioxide (0.500g, 1.54 mmol) was dissolved in dry THF (15mL) in a 100 mL round-bottomed flask equipped with a magnetic stirrer under a nitrogen atmosphere. Potassium tert-butoxide (0.173g, 1.54 mmol) in dry THF (15 mL) was added. The reaction mixture was stirred for three days. water (10 mL) was added. The THF was removed using a rotary evaporator. The residue was extracted with dicholoromethane and then washed with water. The organic layer was dried over anhydrous magnesium sulfate and concentrated to yield a quantitative amount of starting material.

Reaction of 3-Tosyl-1,2,3-benzoxathiazole-2,2-dioxide with Methyllithium . 3-Tosyl-1,2,3-Benzoxathiazole-2,2-dioxide (0.300g, 0.923 mmol) was dissolved in THF (15 mL) in a 50 mL oven-dried three-necked round-bottomed flask equipped wih a magnetic stirrer. The system was flushed with nitrogen. Methyllithium solution (1.32 mL, 2.77 mmol) was added by syringe. The reaction was complete in five min (TLC, Et_2O: Hexane). Eight drops of water were added. The reaction mixture was stirred for another fifteen min. The THF was removed using a rotary evaporator. The residue was extracted with dichloromethane. The dichloromethane layer was dried over anhydrous magnesium sulfate and concentrated to give a solid residue which was

recrystallized from 95% ethanol, 0.0722g (48.8%): mp 132-133 °C (lit[154] 133 °C); IR spectrum no 4931 (KBr) 1325 and 1165 cm^{-1} (s, SO_2); ^1H NMR spectrum no 9968 ($CDCl_3$) δ 8.00-7.70 and 7.50-7.20 (AA'BB', 8H, ArH), 4.65 (s, 2H, CH_2), 2.41 (s, 6H, CH_3); ^{13}C NMR spectrum no 7267 ($CDCl_3$) δ 145.9, 135.4, 129.8, 128.7, 74.5 and 21.6. The compound was identified as ditosyl methane (146) by comparison of the mp[154] and spectra with those in the literature (Sadtler 22053 M (NMR), 49219 (IR)).

Reaction of 3-Tosyl-1,2,3-benzoxathiazole-2,2-dioxide with Sodium Hydroxide. 3-Tosyl-1,2,3-benzoxa thiazole-2,2-dixoide (0.089g, 0.275 mmol) was dissolved in acetonitrile (10 mL). One equivalent of sodium hydroxide solution (0.060N, 4.6 mL) was added with vigorous shaking. No color change was observed. water (5 mL) was then added. The mixture was extracted three times with chloroform (5 mL). The combined extracts were dried over anhydrous sodium sulfate and concentrated using a rotary evaporator to give 0.0307g (35.7%) of starting material. The water layer was concentrated under reduced pressure, washed three times with ether and was dried over phosphorus pentaoxide under vacuum to give a salt 0.045g g (45%): IR spectrum no 4607 (KBr) 3580-3400 (br, H-O), 1310-1160 cm^{-1} (very board with many peaks under it, OSO_3); ^1H NMR spectrum no 5969 (D_2O) δ 7.79-6.75 (m, 8H, ArH), 2.35 (s, 3H, CH_3). Anal. Calcd for

$C_{13}H_{11}NO_6S_2Na_2$: C, 38.05; H, 2.96; N, 3.41. Found: C, 38.38; H, 2.96; N, 3.41. The compound was identified as the disodium monohydrate salt of 2-(N-tosyl) aminophenyl hydrogen sulfate (154).

Reaction of 3-Tosyl-1,2,3-benzoxathiazole-2,2-dioxide with Potassium Fluoride. 3-Tosyl-1,2,3-benzoxathiazole-2,2-dixiode (0.13g, 0.40mmol) was dissolved in acetonitrile (15 mL) and then potassium fluoride (.037og, 0.800 mmol) in water (5 mL) was added. The reaction mixture was stirred overnight and then concentrated using a rotary evaporator. The residue was extracted three times with dichloromethane. The combined extracts were washed twice with water, dried over anhydrous magnesium sulfate, and concentrated to give a light yellow solid, 0.060g (87%): mp 40-41 °C (lit[133] 41-42 °C). All spectral data agreed with published data (Sadtler spectrum 32035 (IR) and 4321M (NMR)) for 4-toluenesulfonyl fluoride (147). ^{19}F NMR spectrum no 7205, δ 142.88 (from trifluoroacetic acid).

3-Tosyl-1,2,3-benzoxathiazole-2,2-dioxide as a Coupling Reagent.[121] 3-Tosyl-1,2,3-benzoxa thiazole-2,2-dioxide (0.163g, 0.500 mmol) in dry THF (5 mL) was added to a mixture of acetic acid (.0280 mL, 0.500 mmol) and triethylamine (0.0697 mL, 0.500 mmol) in dry THF (5 mL) at room temperature. After being stirred for twenty four hours, a solution of benzylamine (0.0535g, 0.500 mmol) in THF (2 mL) was added. After seventy-six hours (TLC) the

solvents were removed under reduced pressure and a 7% aqueous solution of sodium bicarbonate (15 mL) was added to the residue. Extraction with two 15 mL portions of ethyl acetate, washing with four 5 mL portions of bicarbonate, and drying over anhydrous sodium sulfate led to a a light yellow solid of phenyl methylacetamide (169) which was purified on preparative TLC plates using a mixture of diethyl ether and ethyl acetate (2:1 v/v) as eluent: mp 60 °C (lit[121] 60-61 °C); IR spectrum no 4662 (KBr), 3310 (s, NH), 1650 cm^{-1} (s, C=O); ^1H NMR spectrum no 9634 ($CDCl_3$) δ 7.28 (s, 5, ArH), 4.31, (d, 1, NH), 1.91 (s, 3, CH_3). The mp and spectra matched those in the literature.[121]

Kinetic Procedure

Materials. 5-Tosyl-1,2,5-benzoxathiazole was obtained by the synthetic procedure described previously. Carbonate free sodium hydroxide, DILUT-IT Analytical Concentration 0.5N (J.T. Baker), was used as a stock solution. All water used in this work was distilled deionized water. Acetonitrile, spectrophotometric grade (Aldrich), was used for making solutions.

Preparation of the sample solution. The cyclic sulfamide, was weighed (0.011g) and then transferred to a 50 mL volumetric flask. Acetonitrile was then added to fill to the mark (6.77×10^{-4} M).

Preparation of Base. The carbonate free sodium hydroxide was titrated by oxalic acid, using phenolphthalein as an

indicator. The appropriate amount of base stock solution was transferred by pipet to 25 mL volumetric flasks. Then deionized water was used to fill to the mark; 0.05, 0.05, and 0.10N base solution were prepared in this manner.

Method. Kinetic data was gathered by following the appearance of the product peak at 294 nm at 0 , 10 , 20 and 30 ^{o}C. A Cary 219 spectrophotometer equipped with a thermostated cell holder and temperature controlled bath was used to record absorbance changes with time at 0 , 10 and 20 ^{o}C. The kinetic solution was prepared by placing sample solution in the cuvette (0.5 mL) in the thermostated cell holder. The appropriated base solution (2.5 mL) was added quickly by syringe followed by rapid stirring. The adsorbance was recorded vs time. The Durrum-Gibson stopped-flow spectrophotometer with a 0.02 m path length cuvette and a Kel-F flow path, was used to gather the kinetic data at 30 ^{o}C. A linear least-square program and an Apple IIe computer was used to obtain pseudo-first order rate constants.

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APPENDIX

Table 1-36

Kinetic Data Obtained Using a Cary 219 UV Spectropnotometer

The absorbance as afunction of time was plotted as log $(A - A_t) = -k_t/2.303$, A = absorbance, t = time in seconds, on an Apple IIe computer. The rate constant k = -B in unit of 1/s.

0.05N NaOH 0°C

Table 1 Run 1

Time(s)	A(t)	A(t=∞) - A(t)
0	.1450	.1140
10	.1600	.0990
20	.1780	.0810
30	.1900	.0690
40	.2000	.0590
60	.2190	.0400
80	.2300	.0290

Absorbance (t=∞) = .2590
Fitting Parameters;
A = -2.157
B = -.01740
Error of Estimate 0.02760
Correlation Coefficient 0.9675
k_{obsd} = .01740

Table 2 Run 2

Time(s)	A(t)	A(t=∞) - A(t)
0	.1570	.0910
10	.1620	.0860
20	.1780	.0700
30	.1890	.0590
40	.2000	.0480
60	.2150	.0330
80	.2250	.0230

Absorbance (t=∞) = .2480
Fitting Parameters;
A = -2.322
B = -.01800
Error of Estimate 0.06960
Correlation Coefficient 0.9209
k_{obsd} = .01800

Table 3 Run 3

Time(s)	A(t)	A(t=∞) - A(t)
0	.1650	.1000
10	.1780	.0870
20	.1910	.0740
30	.2050	.0600
40	.2180	.0470
60	.2310	.0340
80	.2420	.0230

Absorbance (t=∞) = .2650
Fitting Parameters;
A = -2.268
B = -.01870
Error of Estimate 0.04970
Correlation Coefficient 0.9458
k_{obsd} = .01870

Table 4 Run 4

Time(s)	A(t)	A(t=∞) - A(t)
0	.1450	.1140
10	.1600	.0990
20	.1780	.0810
30	.1900	.0690
40	.2000	.0590
60	.2190	.0400
80	.2300	.0290

Absorbance (t=∞) = .2590
Fitting Parameters;
A = -2.157
B = -.01740
Error of Estimate 0.02760
Correlation Coefficient 0.9675
k_{obsd} = .01740

0.06N NaOH 0°C

Table 5 Run 1

Time(s)	A(t)	A(t=∞) - A(t)
0	.1550	.0860
10	.1700	.0710
20	.1830	.0580
30	.1950	.0460
40	.2050	.0360
60	.2180	.0230
80	.2250	.0160

Absorbance (t=∞) = .2410
Fitting Parameters;
A = -2.441
B = -.02150
Error of Estimate 0.04340
Correlation Coefficient 0.9588
k_{obsd} = .02150

Table 6 Run 2

Time(s)	A(t)	A(t=∞) - A(t)
0	.1510	.1090
10	.1700	.0900
20	.1880	.0720
30	.2000	.0600
40	.2170	.0430
60	.2300	.0300
80	.2400	.0200

Absorbance (t=∞) = .2600
Fitting Parameters;
A = -2.209
B = -.02160
Error of Estimate 0.06460
Correlation Coefficient 0.9387
k_{obsd} = .02160

Table 7 Run 3

Time(s)	A(t)	A(t=∞) - A(t)
0	.1570	.0950
10	.1700	.0820
20	.1880	.0640
30	.1980	.0540
40	.2100	.0420
60	.2250	.0270
80	.2330	.0190

Absorbance (t=∞) = .2520
Fitting Parameters;
A = -2.327
B = -.02070
Error of Estimate 0.05080
Correlation Coefficient 0.9499
k_{obsd} = .02070

Table 8 Run 4

Time(s)	A(t)	A(t=∞) - A(t)
0	.1720	.0910
10	.1850	.0780
20	.1990	.0640
30	.2100	.0530
40	.2200	.0430
60	.2350	.0280
80	.2450	.0180

Absorbance (t=∞) = .2630
Fitting Parameters;
A = -2.352
B = -.02050
Error of Estimate 0.04690
Correlation Coefficient 0.9531
k_{obsd} = .02050

.1N NaOH 0°C

Table 9 Run 1

Time(s)	A(t)	A(t=∞) - A(t)
0	.2390	.0710
6	.2500	.0600
16	.2700	.0400
26	.2800	.0300
36	.2890	.0210
40	.2950	.0150

Absorbance (t=∞) = .3100
Fitting Parameters;
A = -2.609
B = -.03700
Error of Estimate 0.1104
Correlation Coefficient 0.8839
k_{obsd} = .03700

Table 10 Run 2

Time(s)	A(t)	A(t=∞) - A(t)
0	.1620	.0910
4	.1750	.0780
10	.1900	.0630
18	.2050	.0480
26	.2170	.0360
40	.2300	.0230

Absorbance (t=∞) = .2530
Fitting Parameters;
A = -2.413
B = -.03440
Error of Estimate 0.02120
Correlation Coefficient 0.9739
k_{obsd} = .03440

Table 11 Run 3

Time(s)	A(t)	A(t=∞) - A(t)
0	.1300	.0800
4	.1400	.0700
10	.1520	.0580
20	.1690	.0410
30	.1800	.0300
42	.1900	.0200

Absorbance (t=∞) = .2100
Fitting Parameters;
A = -2.525
B = -.03300
Error of Estimate 0.02900
Correlation Coefficient 0.9077
k_{obsd} = .03300

Table 12 Run 4

Time(s)	A(t)	A(t=∞) - A(t)
0	.1110	.1040
4	.1270	.0880
10	.1450	.0700
20	.1680	.0470
30	.1850	.0300
40	.1950	.0200

Absorbance (t=∞) = .2150
Fitting Parameters;
A = -2.256
B = -.04130
Error of Estimate 0.02211
Correlation Coefficient 0.9783
k_{obsd} = .04130

.05N NaOH 10°C

Table 13 Run 1

Time(s)	A(t)	A(t=∞) - A(t)
1	.1950	.1830
4	.2050	.0730
8	.2150	.0630
13	.2290	.0490
18	.2390	.0390
23	.2460	.0320
30	.2550	.0230

Absorbance (t=∞) = .2780
Fitting Parameters;
A = -2.435
B = -.04440
Error of Estimate 0.02350
Correlation Coefficient 0.9709
k_{obsd} = .04440

Table 14 Run 2

Time(s)	A(t)	A(t=∞) - A(t)
1	.170	.1100
4	.1810	.0990
7	.1910	.0890
10	.2030	.0770
14	.2150	.0650
18	.2250	.0550
22	.2350	.0450
28	.2450	.0350
35	.2550	.0250
46	.2650	.0150

Absorbance (t=∞) = .2800
Fitting Parameters;
A = -2.123
B = -.04460
Error of Estimate 0.04400
Correlation Coefficient 0.9678
k_{obsd} = .04460

Table 15 Run 3

Time(s)	A(t)	A(t=∞) - A(t)
1	.1856	.0970
4	.1980	.0840
7	.2090	.0730
11	.2210	.0610
15	.2310	.0510
20	.2410	.0410
28	.2540	.0280
38	.2650	.0170

Absorbance (t=∞) = .2820
Fitting Parameters;
A = -2.283
B = -.04660
Error of Estimate 0.02810
Correlation Coefficient 0.9749
k_{obsd} = .04660

Table 16 Run 4

Time(s)	A(t)	A(t=∞) - A(t)
1	.1690	.1030
4	.1820	.0900
7	.1920	.0800
12	.2040	.0680
17	.2180	.0640
22	.2290	.0430
27	.2370	.0350
37	.2500	.0220

Absorbance (t=∞) = .2720
Fitting Parameters;
A = -2.217
B = -.04250
Error of Estimate 0.4240
Correlation Coefficient 0.9568
k_{obsd} = .04250

.06N NaOH 10°C

Table 17 Run 1

Time(s)	A(t)	A(t=∞) - A(t)
1	.1750	.0970
4	.1850	.0870
8	.2000	.0720
12	.2100	.0620
15	.2200	.0520
18	.2300	.0420
23	.2400	.0320
29	.2500	.0220

Absorbance (t=∞) = .2720
Fitting Parameters;
A = -2.214
B = -.05330
Error of Estimate 0.9070
Correlation Coefficient 0.9047
k_{obsd} = .05330

Table 18 Run 2

Time(s)	A(t)	A(t=∞) - A(t)
1	.2000	.0800
4	.2100	.0700
6	.2200	.0600
10	.2300	.0500
14	.2400	.0400
19	.2500	.0300
26	.2600	.0200

Absorbance (t=∞) = .2800
Fitting Parameters;
A = -2.474
B = -.05460
Error of Estimate 0.3120
Correlation Coefficient 0.9635
k_{obsd} = .05460

Table 19 Run 4

Time(s)	A(t)	A(t=∞) - A(t)
1	.2180	.0670
4	.2280	.0570
8	.2390	.0460
13	.2500	.0350
20	.2600	.0250
28	.2700	.0150

Absorbance (t=∞) = .2850
Fitting Parameters;
A = -2.641
B = -.05460
Error of Estimate 0.3830
Correlation Coefficient 0.9566
k_{obsd} = .05460

Table 20 Run 5

Time(s)	A(t)	A(t=∞) - A(t)
1	.2100	.0740
4	.2200	.0640
8	.2300	.0540
12	.2400	.0440
17	.2500	.0340
24	.2600	.0240
28	.2700	.0140

Absorbance (t=∞) = .2840
Fitting Parameters;
A = -2.524
B = -.05161
Error of Estimate 0.05030
Correlation Coefficient 0.9507
k_{obsd} = .05161

0.1ON NaOH 10°C

Table 21 Run 1

Time(s)	A(t)	A(t=∞) - A(t)
1	.1320	.1330
3	.1410	.1240
6	.2050	.0600
9	.2200	.0450
13	.0320	.0330
16	.2400	.0250

Absorbance (t=∞) = .2650
Fitting Parameters;
A = -2.306
B = -.08620
Error of Estimate 0.1132
Correlation Coefficient 0.8754
k_{obsd} = .08620

Table 22 Run 2

Time(s)	A(t)	A(t=∞) - A(t)
1	.1400	.1230
3	.1550	.1080
5	.1740	.0890
7	.1900	.0730
9	.2020	.0610
12	.2180	.0450
14	.2250	.0380
17	.2350	.0280
22	.2450	.0180

Absorbance (t=∞) = .2630
Fitting Parameters;
A = -1.967
B = -.09350
Error of Estimate 0.03664
Correlation Coefficient 0.9715
k_{obsd} = .09350

Table 23 Run 3

Time(s)	A(t)	A(t=∞) - A(t)
1	.1700	.1200
3	.1850	.1050
5	.2000	.0906
7	.2130	.0770
10	.2300	.0600
13	.2420	.0480
16	.2500	.0400
21	.2650	.0250

Absorbance (t=∞) = .2900
Fitting Parameters;
A = -2.026
B = -.07760
Error of Estimate 0.04460
Correlation Coefficient 0.9552
k_{obsd} = .07760

Table 24 Run 4

Time(s)	A(t)	A(t=∞) - A(t)
1	.1490	.1060
3	.1650	.0900
11	.2100	.0450
15	.2240	.0310
20	.2350	.0200

Absorbance (t=∞) = .2550
Fitting Parameters;
A = -2.146
B = -.08800
Error of Estimate 0.1340
Correlation Coefficient 0.9856
k_{obsd} = .08800

.05N NaOH 20°C

Table 25 Run 1

Time(s)	A(t)	A(t=∞) - A(t)
1	.1400	.1730
2	.1600	.1530
3	.1730	.1400
6	.2000	.1130
8	.2200	.0930
10	.2340	.0790
12	.2480	.0650
15	.2650	.0480
20	.2810	.0320

Absorbance (t=∞) = .3130
Fitting Parameters;
A = -1.677
B = -.08840
Error of Estimate 0.4320
Correlation Coefficient 0.9617
k_{obsd} = .08840

Table 26 Run 2

Time(s)	A(t)	A(t=∞) - A(t)
1	.1400	.1800
2	.1600	.1600
3	.1750	.1450
4	.1900	.1300
6	.2110	.1090
8	.2230	.0970
10	.2370	.0830
12	.2500	.0700
15	.2680	.0520
21	.2900	.0300

Absorbance (t=∞) = .3200
Fitting Parameters;
A = -1.656
B = -.08680
Error of Estimate 0.6210
Correlation Coefficient 0.9473
k_{obsd} = .08680

Table 27 Run 3

Time(s)	A(t)	$A(t=\infty) - A(t)$
1	.1500	.1680
2	.1700	.1480
3	.1850	.1330
5	.2110	.1070
8	.2350	.0830
11	.2500	.0680
14	.2680	.0500
18	.2810	.0370
22	.2910	.0270

Absorbance ($t=\infty$) = .3180
Fitting Parameters;
A = -1.757
B = -.08590
Error of Estimate 0.7390
Correlation Coefficient 0.9423
k_{obsd} = .08590

Table 28 Run 4

Time(s)	A(t)	$A(t=\infty) - A(t)$
1	.1700	.1580
2	.1850	.1430
3	.2000	.1280
5	.2250	.1030
8	.2450	.0830
11	.2620	.0660
14	.2790	.0490
17	.2900	.0380
22	.3020	.0260

Absorbance ($t=\infty$) = .3280
Fitting Parameters;
A = -1.794
B = -.08570
Error of Estimate 0.5640
Correlation Coefficient 0.9551
k_{obsd} = .08570

.06N NaOH 20°C

Table 29 Run 1

Time(s)	A(t)	A(t=∞) - A(t)
1	.1500	.1290
2	.1720	.1070
4	.1980	.0810
8	.2220	.0570
10	.2310	.0480
14	.2490	.0300
18	.2600	.0190

Absorbance (t=∞) = .2790
Fitting Parameters;
A = -1.200
B = -.1082
Error of Estimate 0.8010
Correlation Coefficient 0.9227
k_{obsd} = .1082

Table 30 Run 2

Time(s)	A(t)	A(t=∞) - A(t)
1	.1700	.1450
2	.1900	.1250
3	.2010	.1140
5	.2320	.0830
8	.2520	.0630
11	.2630	.0520
14	.2800	.0350
18	.2900	.0250

Absorbance (t=∞) = .3150
Fitting Parameters;
A = -1.888
B = -.1021
Error of Estimate 0.1037
Correlation Coefficient 0.9119
k_{obsd} = .1021

Table 31 Run 3

Time(s)	A(t)	A(t=∞) - A(t)
1	.1500	.1560
2	.1700	.1360
3	.1900	.1160
4	.2100	.0960
6	.2320	.0740
9	.2500	.0560
14	.2700	.0360
19	.2850	.0210

Absorbance (t=∞) = .3060
Fitting Parameters;
A = -1.841
B = -.1085
Error of Estimate 0.1354
Correlation Coefficient 0.8957
k_{obsd} = .1085

Table 32 Run 4

Time(s)	A(t)	A(t=∞) - A(t)
1	.1600	.1610
2	.1820	.1390
3	.2010	.1200
5	.2230	.0980
7	.2390	.0820
10	.2600	.0610
14	.2800	.0410
18	.2950	.0260

Absorbance (t=∞) = .3210
Fitting Parameters;
A = -1.770
B = -.1037
Error of Estimate 0.05490
Correlation Coefficient 0.0534
k_{obsd} = .1037

.10N NaOH 20°C

Table 33 Run 1

Time(s)	A(t)	A(t=∞) - A(t)
1	.2150	.0940
2	.2330	.0760
3	.2500	.0590
5	.2700	.0390
9	.2800	.0290
12	.2900	.0190

Absorbance (t=∞) = .3090
Fitting Parameters;
A = -2.161
B = -.2238
Error of Estimate 0.1637
Correlation Coefficient 0.8714
k_{obsd} = .2238

Table 34 Run 2

Time(s)	A(t)	A(t=∞) - A(t)
1	.2100	.1150
2	.2390	.0860
3	.2550	.0700
5	.2760	.0490
8	.2900	.0350
12	.3050	.0200

Absorbance (t=∞) = .3250
Fitting Parameters;
A = -2.141
B = -.1518
Error of Estimate 0.1359
Correlation Coefficient 0.8654
k_{obsd} = .1518

Table 35 Run 3

Time(s)	A(t)	A(t=∞) - A(t)
1	.1800	.1320
2	.2050	.1070
3	.2110	.1010
4	.2390	.0730
5	.2550	.0570
7	.2700	.0420
10	.2830	.0290
13	.2930	.0190

Absorbance (t=∞) = .3120
Fitting Parameters;
A = -1.921
B = -.1631
Error of Estimate 0.1637
Correlation Coefficient 0.8714
k_{obsd} = .1631

Table 36 Run 4

Time(s)	A(t)	A(t=∞) - A(t)
1	.2000	.1310
2	.2300	.1010
3	.2450	.0860
5	.2750	.0560
8	.2950	.0360
12	.3100	.0210

Absorbance (t=∞) = .3310
Fitting Parameters;
A = -1.958
B = -.1646
Error of Estimate 0.1135
Correlation Coefficient 0.8959
k_{obsd} = .1646

Table 37-56

Kinetic Data Obtained Using a Durrum-Gibson Stopped-flow Spectrophotometer

.082N NaOH 30°C

Table 37 Run 1 1s/dev^{-1}

$I_0 \rightarrow I_{100}$ = 61.00 mm

$I_0 \rightarrow I_\infty$ = 12.50 mm

time(s)	$I_\infty - I_t$	$I_0 - I_t$	%T	Ab(t)	A(∞)-A(t)
0	23.50	36.00	59.00	0.2290	0.4595
2	22.20	34.70	56.88	0.2450	0.4435
7	18.50	31.00	50.82	0.2940	0.3945
9	16.50	29.00	47.54	0.3229	0.3656
12	14.50	27.00	44.26	0.3540	0.3345
17	11.50	24.00	39.34	0.4052	0.2833
22	9.90	22.40	36.72	0.4351	0.2534
27	8.50	21.00	34.43	0.4631	0.2254
32	7.50	20.00	32.79	0.4841	0.2044
37	6.50	19.00	31.15	0.5065	0.1820

%T (t=∞) = 20.49
A(t=∞) = 0.6885
Fitting Parameters;
A = -0.7780
B = -0.02580
Error of Estimate .05100
Correlation Coefficient .9268
k_{obsd} = 0.1290

Table 38 Run 2 $2s/dev^{-1}$

$I_0 \rightarrow I_{100}$ = 61.00 mm

$I_0 \rightarrow I_\infty$ = 7.00 mm

time(s)	$I_\infty - I_t$	$I_0 - I_t$	%T	Ab(t)	$A(\infty) - A(t)$
0	18.50	25.50	41.80	0.3788	0.5613
2	16.00	23.00	37.70	0.4237	0.5164
4	13.50	20.50	33.61	0.4735	0.4666
7	10.50	17.50	28.69	0.5423	0.3978
9	9.50	16.50	27.05	0.5678	0.3723
12	8.00	15.00	24.59	0.6092	0.3309
17	6.00	13.00	21.31	0.6714	0.2683
22	4.50	11.50	18.85	0.7247	0.2154
27	3.50	10.50	17.21	0.7642	0.1759
32	2.50	9.50	15.57	0.8077	0.1324
37	1.50	8.50	13.93	0.8560	0.0841

%T ($t=\infty$) = 11.48
$A(t=\infty)$ = 0.9401
Fitting Parameters;
A = -0.5518
B = -0.04750
Error of Estimate .1555
Correlation Coefficient .8848
k_{obsd} = 0.1188

Table 39 Run 3 $2s/dev^{-1}$

$I_0 \rightarrow I_{100}$ = 61.00 mm

$I_0 \rightarrow I_\infty$ = 21.50 mm

time(s)	$I_\infty - I_t$	$I_0 - I_t$	%T	Ab(t)	$A(\infty) - A(t)$
0	19.50	41.00	67.21	0.1726	0.2802
2	16.50	38.00	62.30	0.2055	0.2473
4	13.50	35.00	57.38	0.2412	0.2116
7	10.50	32.00	52.46	0.2802	0.1726
9	9.50	31.00	50.82	0.2940	0.1588
12	7.50	29.00	47.54	0.3229	0.1299
17	4.80	26.30	43.11	0.3654	0.0874
22	3.50	25.00	40.98	0.3824	0.0654
27	2.50	24.00	39.34	0.4052	0.0476
32	1.50	23.00	37.70	0.4237	0.0291

%T (t=∞) = 35.25
A(t=∞) = 0.4528
Fitting Parameters;
A = -1.255
B = -0.6870
Error of Estimate .09168
Correlation Coefficient .9426
k_{obsd} = 0.1776

Table 40 Run 4 $2s/dev^{-1}$

$I_0 \rightarrow I_{100}$ = 61.00 mm

$I_0 \rightarrow I_\infty$ = 12.10 mm

time(s)	$I_\infty - I_t$	$I_0 - I_t$	%T	Ab(t)	$A(\infty) - A(t)$
0	22.50	34.60	56.72	0.2463	.4562
2	19.50	31.60	51.80	0.2856	.4169
4	16.50	28.60	46.89	0.3289	.3736
7	13.50	25.60	41.97	0.3771	.3254
9	11.50	23.60	38.69	0.4124	.2901
12	9.10	21.20	34.75	0.4590	.2435
17	6.50	18.60	30.49	0.5158	.1864
22	4.50	16.60	27.21	0.5653	.1372
27	3.50	15.60	25.57	0.5922	.1103
32	2.50	14.60	23.93	0.6211	.0814

%T ($t=\infty$) = 19.84
$A(t=\infty)$ = 0.7025
Fitting Parameters;
A = -.7645
B = -.05420
Error of Estimate .03640
Correlation Coefficient .9710
k_{obsd} = 0.1354

Table 41 Run 5 $2s/dev^{-1}$

$I_0 \rightarrow I_{100}$ = 61.00 mm

$I_0 \rightarrow I_\infty$ = 5.00 mm

time(s)	$I_\infty - I_t$	$I_0 - I_t$	%T	Ab(t)	A(∞)-A(t)
0	22.50	27.50	45.08	0.3460	0.7402
2	20.50	25.50	41.80	0.3788	0.7024
4	17.50	22.50	36.89	0.4331	0.6531
7	13.50	18.50	30.33	0.5181	0.5681
9	11.50	16.50	27.05	0.5678	0.5184
12	9.50	14.50	23.77	0.6240	0.4622
17	6.90	11.90	19.51	0.7097	0.3765
22	5.00	10.00	16.39	0.7854	0.3008
27	4.00	9.00	14.75	0.8312	0.2550
32	3.00	8.00	13.11	0.8824	0.2038

%T (t=∞) = 8.200
A(t=∞) = 1.086
Fitting Parameters;
A = -.2802
B = -.04090
Error of Estimate .03040
Correlation Coefficient .9680
k_{obsd} = 0.1023

Table 42 Run 6 $2s/dev^{-1}$

$I_0 \rightarrow I_{100}$ = 61.00 mm

$I_0 \rightarrow I_\infty$ = 22.20 mm

time(s)	$I_\infty - I_t$	$I_0 - I_t$	%T	Ab(t)	$A(\infty) - A(t)$
0	21.50	43.70	71.64	0.1448	0.2942
2	18.50	40.70	66.72	0.1757	0.2633
4	15.50	37.70	61.80	0.2090	0.2300
6	13.00	35.20	57.70	0.2388	0.2002
9	10.50	32.70	53.61	0.2708	0.1682
11	8.90	31.10	50.98	0.2926	0.1464
16	6.00	28.20	46.23	0.3351	0.1039
21	4.50	26.70	43.77	0.3588	0.0802
26	3.50	25.70	42.13	0.3754	0.0636
31	2.50	24.70	40.49	0.3927	0.0463
36	1.50	23.70	38.85	0.4106	0.0284

%T (t=∞) = 36.39
A(t=∞) = .4390
Fitting Parameters;
A = -1.242
B = -.05980
Error of Estimate 0.06692
Correlation Coefficient .9501
k_{obsd} = 0.1494

Table 43 Run 7 $2s/dev^{-1}$

$I_0 \rightarrow I_{100}$ = 61.00 mm

$I_0 \rightarrow I_\infty$ = 2.00 mm

time(s)	$I_\infty - I_t$	$I_0 - I_t$	%T	Ab(t)	$A(\infty) - A(t)$
0	22.25	24.25	39.75	0.4007	1.0834
2	19.25	21.25	34.84	0.4579	1.0262
4	16.75	18.70	30.74	0.5123	0.9718
6	14.00	16.00	26.23	0.5812	0.9029
9	11.25	13.25	21.72	0.6631	0.8210
11	9.75	11.75	19.26	0.7153	0.7688
16	6.95	8.95	14.67	0.8336	0.6505
21	5.05	7.05	11.56	0.9370	0.5471
26	3.75	5.75	9.43	1.0255	0.4586
31	3.00	5.00	8.20	1.0862	0.3979
36	2.25	4.25	6.97	1.1568	0.3273

%T ($t=\infty$) = 3.280
A($t=\infty$) = 1.484
Fitting Parameters;
A = -.09410
B = -.0330
Error of Estimate .01860
Correlation Coefficient .9749
k_{obsd} = .08250

Table 44 Run 8 $1s/dev^{-1}$

$I_0 \rightarrow I_{100}$ = 61.00 mm

$I_0 \rightarrow I_\infty$ = 23.00 mm

time(s)	$I_\infty - I_t$	$I_0 - I_t$	%T	Ab(t)	A(∞)-A(t)
0	23.20	46.2	75.74	0.1200	0.3036
2	21.50	44.5	72.95	0.1369	0.2867
4	20.00	43.0	70.49	0.1518	0.2718
7	17.90	40.9	67.05	0.1736	0.2500
9	16.50	39.5	64.75	0.1887	0.2349
12	14.90	37.9	62.13	0.2066	0.2170
17	12.50	35.5	58.20	0.2350	0.1886
22	10.50	33.5	54.92	0.2602	0.1634
27	9.00	32.0	52.46	0.2801	0.1435
32	7.50	30.5	50.0	0.3010	0.1226
37	6.50	29.5	48.36	0.3155	0.1081

%T (t=∞) = 37.70
A(t=∞) = .4236
Fitting Parameters;
A = -1.1923
B = -.02800
Error of Estimate .01010
Correlation Coefficient .9872
k_{obsd} = 0.1400

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Table 45 Run 1 ls/dev^{-1}

$I_0 \rightarrow I_{100}$ = 61.00 mm

$I_0 \rightarrow I_\infty$ = 18.50 mm

time(s)	$I_\infty - I_t$	$I_0 - I_t$	%T	Ab(t)	A(∞)-A(t)
0	21.00	39.50	64.75	0.1888	0.3243
4	18.00	36.50	59.84	0.2230	0.2951
7	15.50	34.00	55.74	0.2538	0.2643
10	13.50	32.00	52.46	0.2801	0.2380
14	10.50	29.00	47.54	0.3229	0.1952
19	8.50	27.00	44.26	0.3540	0.1641
24	6.50	25.00	40.98	0.3874	0.1307
29	5.00	23.50	38.52	0.4143	0.1038
34	4.50	23.00	37.70	0.4237	0.0944
39	3.50	22.00	36.07	0.4429	0.0752
44	2.50	21.00	34.43	0.4631	0.0550

%T (t=∞) = 30.33
A(t=∞) = .5181
Fitting Parameters;
A = -1.079
B = -.03890
Error of Estimate .06550
Correlation Coefficient .9401
k_{obsd} = .1945

Table 46 Run 2 $1s/dev^{-1}$

$I_0 \rightarrow I_{100}$ = 61.00 mm

$I_0 \rightarrow I_\infty$ = 12.10 mm

time(s)	$I_\infty - I_t$	$I_0 - I_t$	%T	Ab(t)	A(∞)-A(t)
0	21.50	33.60	55.08	0.2590	0.4435
4	19.50	31.60	51.80	0.2857	0.4168
7	16.50	28.10	46.89	0.3289	0.3736
10	14.50	26.60	43.61	0.3604	0.3421
14	11.50	23.60	38.69	0.4124	0.2901
19	9.00	21.10	34.59	0.4610	0.2415
24	7.00	19.10	31.31	0.5043	0.1982
29	5.50	17.10	28.03	0.5524	0.1501
34	4.50	16.60	27.21	0.5653	0.1372
39	3.50	15.60	25.57	0.5923	0.1102
44	2.50	14.60	23.93	0.6211	0.0814

%T (t=∞) = 19.84
A(t=∞) = .7025
Fitting Parameters;
A = -.7390
B = -.03730
Error of Estimate .08740
Correlation Coefficient .9169
k_{obsd} = .1867

Table 47 Run 3 $1s/dev^{-1}$

$I_0 \rightarrow I_{100}$ = 61.00 mm

$I_0 \rightarrow I_\infty$ = 9.00 mm

time(s)	$I_\infty - I_t$	$I_0 - I_t$	%T	Ab(t)	$A(\infty) - A(t)$
0	20.50	29.50	48.36	0.3155	0.5157
2	18.50	27.50	45.08	0.3460	0.4852
5	16.00	25.50	41.80	0.3788	0.4524
8	13.50	22.50	36.88	0.4332	0.3980
10	12.50	21.50	35.24	0.4530	0.3782
15	9.50	18.50	30.33	0.5181	0.3131
20	8.00	17.00	27.87	0.5549	0.2763
25	6.50	15.50	25.41	0.5950	0.2362
30	5.00	14.00	22.95	0.6392	0.1920
35	4.50	13.50	22.13	0.6550	0.1762
40	3.80	12.80	20.98	0.6782	0.1530

%T ($t=\infty$) = 14.75
$A(t=\infty)$ = 0.8312
Fitting Parameters;
A = -.6546
B = -.03140
Error of Estimate .06430
Correlation Coefficient .9316
k_{obsd} = .1568

Table 48 Run 4 ls/dev^{-1}

$I_0 \rightarrow I_{100}$ = 61.00 mm

$I_0 \rightarrow I_\infty$ = 5.50 mm

time(s)	$I_\infty - I_t$	$I_0 - I_t$	%T	Ab(t)	A(∞)-A(t)
0	21.50	27.00	44.26	0.3540	0.6908
4	19.50	25.00	40.98	0.3874	0.6574
7	16.50	22.00	36.07	0.4429	0.6019
10	14.00	19.50	31.97	0.4953	0.5495
14	10.80	16.30	26.72	0.5732	0.4716
19	9.00	14.50	23.77	0.6240	0.4208
24	7.00	12.50	20.49	0.6885	0.3563
29	5.50	11.00	18.03	0.7440	0.3008
34	4.50	10.00	16.39	0.7854	0.2594
39	3.50	9.00	14.75	0.8312	0.2136
44	3.00	8.50	13.93	0.8560	0.1888

%T (t=∞) = 9.020
A(t=∞) = 1.045
Fitting Parameters;
A = -.3115
B = -.0307
Error of Estimate .05850
Correlation Coefficient .9322
k_{obsd} = .1535

Table 49 Run 5 1s dev^{-1}

$I_0 \rightarrow I_{100}$ = 61.00 mm

$I_0 \rightarrow I_\infty$ = 17.50 mm

time(s)	$I_\infty - I_t$	$I_0 - I_t$	%T	Ab(t)	A(∞)-A(t)
0	20.00	37.50	61.48	0.2113	0.3310
2	18.50	36.00	59.02	0.2290	0.3133
4	17.00	34.50	56.56	0.2475	0.2948
7	15.00	32.50	53.28	0.2734	0.2689
12	11.50	29.00	47.54	0.3229	0.2194
17	9.50	27.00	44.26	0.3540	0.1883
22	7.50	25.00	40.98	0.3874	0.1549
27	5.50	23.00	37.70	0.4237	0.1186
32	4.50	22.00	36.07	0.4429	0.0994
37	3.50	21.00	34.43	0.4631	0.0792
42	3.00	20.50	33.61	0.4735	0.0688

%T (t=∞) = 28.69
A(t=∞) = 0.5423
Fitting Parameters;
A = -1.064
B = -.3086
Error of Estimate .07170
Correlation Coefficient .9436
k_{obsd} = .1543

Table 50 Run 6 $1s/dev^{-1}$

$I_0 \rightarrow I_{100}$ = 61.00 mm

$I_0 \rightarrow I_\infty$ = 11.00 mm

time(s)	$I_\infty - I_t$	$I_0 - I_t$	%T	Ab(t)	$A(\infty) - A(t)$
0	21.50	32.50	53.28	0.2734	0.4706
2	19.50	30.50	50.00	0.3010	0.4430
4	17.50	28.50	46.72	0.3305	0.4135
7	15.50	26.50	43.44	0.3621	0.3819
12	12.50	23.50	38.52	0.4143	0.3297
17	9.90	20.50	33.61	0.4735	0.2705
22	7.90	18.90	30.98	0.5089	0.2351
27	6.00	17.00	27.87	0.5544	0.1891
32	5.00	16.00	26.23	0.5812	0.1628
37	4.50	15.50	25.41	0.5950	0.1490
42	3.50	14.50	23.77	0.6240	0.1200

%T ($t=\infty$) = 18.03
$A(t=\infty)$ = 0.7440
Fitting Parameters;
A = -.7464
B = -.03250
Error of Estimate .05420
Correlation Coefficient .9494
k_{obsd} = .1625

Table 51 Run 7 $1s/dev^{-1}$

$I_0 \rightarrow I_{100}$ = 61.00 mm

$I_0 \rightarrow I_\infty$ = 5.50 mm

time(s)	$I_\infty - I_t$	$I_0 - I_t$	%T	Ab(t)	$A(\infty) - A(t)$
0	21.50	27.00	44.26	0.3540	0.6908
2	19.50	25.00	40.98	0.3874	0.6574
4	18.00	23.50	38.52	0.4143	0.6305
7	15.50	21.00	34.43	0.4631	0.5817
12	11.50	17.00	27.87	0.5549	0.4899
17	9.50	15.00	24.59	0.6092	0.4356
22	7.50	13.00	21.31	0.6714	0.3734
27	6.00	11.50	18.85	0.7247	0.3201
32	4.90	10.40	17.05	0.7683	0.2765
37	4.00	9.50	15.57	0.8077	0.2371

%T (t=∞) = 9.020
A(t=∞) = 1.045
Fitting Parameters;
A = -.3534
B = -.02910
Error of Estimate .02460
Correlation Coefficient .9696
k_{obsd} = .1455

Table 52 Run 8 $1s/dev^{-1}$

$I_0 \rightarrow I_{100}$ = 61.00 mm

$I_0 \rightarrow I_\infty$ = 16.50 mm

time(s)	$I_\infty - I_t$	$I_0 - I_t$	%T	Ab(t)	$A(\infty) - A(t)$
0	18.50	35.00	57.38	0.2412	0.3566
2	17.00	33.50	54.92	0.2603	0.3275
5	14.60	31.10	50.98	0.2926	0.2952
8	13.00	29.50	48.36	0.3155	0.2723
10	11.50	28.00	45.90	0.3382	0.2496
15	9.10	25.60	41.97	0.3771	0.2107
20	7.00	23.50	38.52	0.4143	0.1735
25	5.50	22.00	36.07	0.4429	0.1449
30	4.50	21.00	34.43	0.4631	0.1247
35	3.70	20.20	33.11	0.4800	0.1078
40	3.00	19.50	31.97	0.4953	0.0925

%T ($t=\infty$) = 27.05
$A(t=\infty)$ = 0.5878
Fitting Parameters;
A = -1.049
B = -0.03430
Error of Estimate .03230
Correlation Coefficient .9633
k_{obsd} = .1714

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Table 53 Run 1 ls/dev^{-1}

$I_0 \rightarrow I_{100}$ = 61.00 mm

$I_0 \rightarrow I_\infty$ = 20.00 mm

time(s)	$I_\infty - I_t$	$I_0 - I_t$	%T	Ab(t)	A(∞)-A(t)
0	19.00	39.00	63.93	0.1943	0.2900
2	16.50	36.50	59.84	0.2230	0.2613
4	14.90	34.50	56.56	0.2475	0.2368
7	12.00	32.00	52.46	0.2787	0.2056
12	9.00	29.00	47.54	0.3229	0.1614
17	6.50	26.50	43.44	0.3621	0.1222
22	4.60	24.60	40.33	0.3944	0.0899
27	3.50	23.50	38.52	0.4143	0.0700
32	2.50	22.50	36.89	0.4331	0.0512
37	2.00	22.00	36.07	0.4429	0.4141
42	1.50	21.50	35.25	0.4528	0.0315

%T (t=∞) = 32.79
A(t=∞) = 0.4843
Fitting Parameters;
A = -1.2192
B = -.05350
Error of Estimate .04980
Correlation Coefficient .9666
k_{obsd} = .2675

Table 54 Run 2 $1s/dev^{-1}$

$I_0 \rightarrow I_{100}$ = 61.00 mm

$I_0 \rightarrow I_\infty$ = 20.00 mm

time(s)	$I_\infty - I_t$	$I_0 - I_t$	%T	Ab(t)	A(∞)-A(t)
0	17.00	37.00	60.66	0.2171	0.2672
2	14.50	34.50	56.56	0.2475	0.2368
5	12.50	32.50	53.28	0.2734	0.2109
8	9.50	29.50	48.36	0.3155	0.1688
10	8.50	28.50	46.72	0.3305	0.1538
15	6.00	26.00	42.62	0.3704	0.1139
20	4.50	24.50	40.16	0.3962	0.0881
25	3.50	23.50	38.52	0.4143	0.0700
30	2.50	22.50	36.89	0.4331	0.0512
35	2.00	22.00	36.07	0.4428	0.0415
40	1.50	21.50	35.25	0.4528	0.0315

%T (t=∞) = 32.79
A(t=∞) = 0.4843
Fitting Parameters;
A = -1.330
B = -.05390
Error of Estimate .05500
Correlation Coefficient .9603
k_{obsd} = .2695

Table 55 Run 3 $1s/dev^{-1}$

$I_0 \rightarrow I_{100}$ = 61.00 mm

$I_0 \rightarrow I_\infty$ = 20.00 mm

time(s)	$I_\infty - I_t$	$I_0 - I_t$	%T	Ab(t)	$A(\infty) - A(t)$
0	19.60	34.10	55.90	0.2526	0.3714
2	16.50	31.10	50.98	0.2926	0.3314
5	13.50	28.00	45.90	0.3382	0.2858
8	11.00	25.50	41.80	0.3788	0.2452
10	9.50	24.00	39.34	0.4052	0.2188
15	7.00	21.50	35.25	0.4528	0.1712
20	5.00	19.50	31.97	0.4952	0.1288
25	3.50	18.00	29.51	0.5300	0.0940

%T (t=∞) = 23.77
A(t=∞) = 0.6240
Fitting Parameters;
A = -.9820
B = -.05410
Error of Estimate .03390
Correlation Coefficient .9619
k_{obsd} = .2703

Table 56 Run 4 $1s/dev^{-1}$

$I_0 \rightarrow I_{100}$ = 61.00 mm

$I_0 \rightarrow I_\infty$ = 20.00 mm

time(s)	$I_\infty - I_t$	$I_0 - I_t$	%T	Ab(t)	A(∞)-A(t)
0	19.50	27.50	45.08	0.3460	0.5364
2	16.50	24.50	40.16	0.3962	0.4862
5	13.50	21.50	35.25	0.4528	0.4296
8	10.90	18.90	30.98	0.5089	0.3735
10	9.50	17.50	28.69	0.5423	0.3401
15	6.50	14.50	23.77	0.6240	0.2584
20	5.00	13.50	22.13	0.6550	0.2274
25	4.00	12.00	19.67	0.7062	0.1762
30	3.00	11.00	18.03	0.7440	0.1384
35	2.00	10.00	16.39	0.7854	0.0970
40	1.50	9.50	15.57	0.8077	0.0747

%T (t=∞) = 13.11
A(t=∞) = 0.8824
Fitting Parameters;
A = -.6299
B = -.04461
Error of Estimate .0496
Correlation Coefficient .9469
k_{obsd} = .2231